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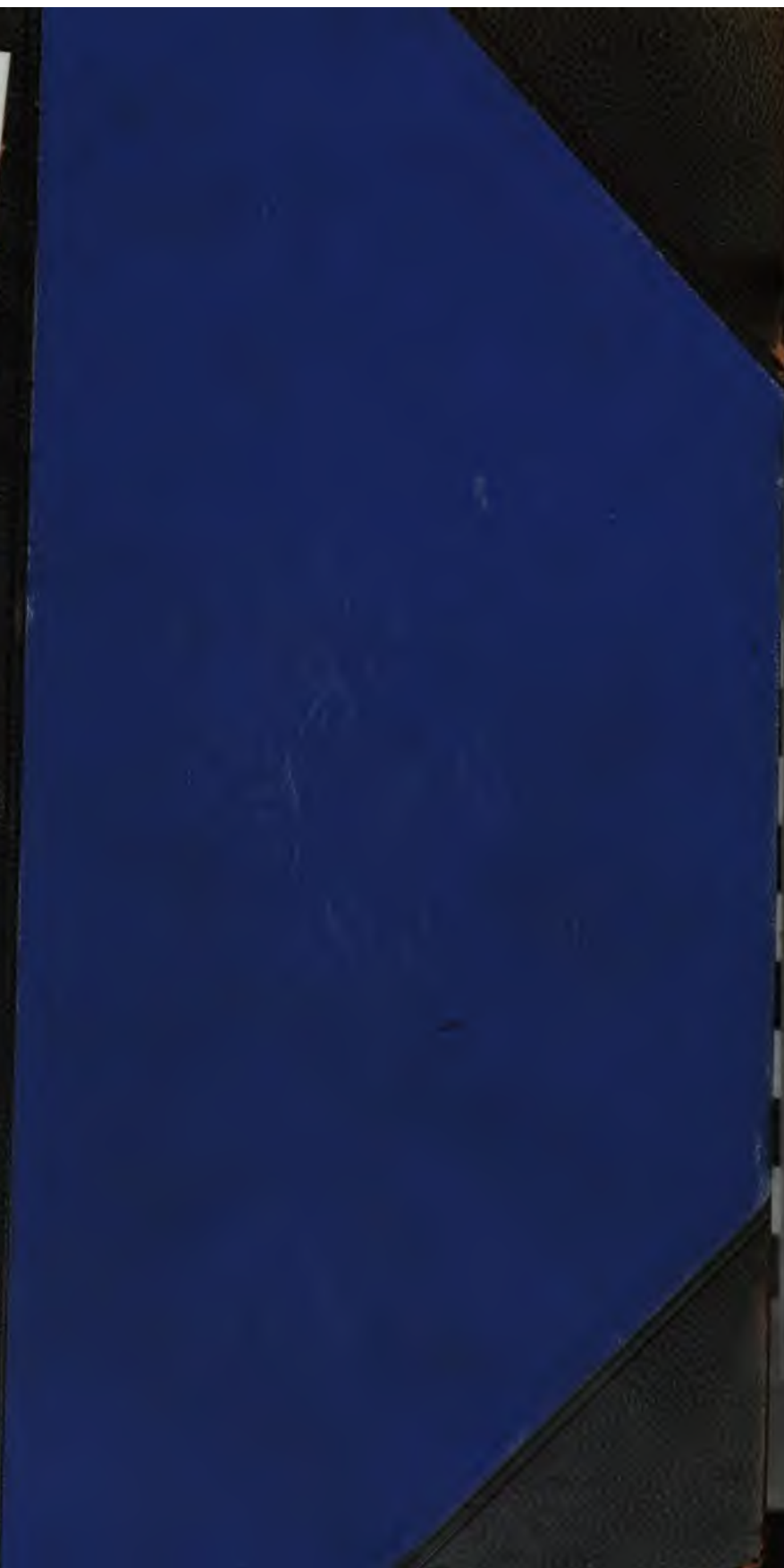
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# The Journal

—OF THE—

## AMERICAN CHEMICAL SOCIETY.

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VOLUME XI.

1889.

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*COMMITTEE ON PAPERS AND PUBLICATIONS :*

A. C. HALE,  
J. F. GEISLER,  
A. A. BRENNEMAN, Editor.

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2. The second part of the document is a list of the names of the persons who were absent from the meeting.

3. The third part of the document is a list of the names of the persons who were present at the meeting.

REGULAR MEETING, January 5th, 1889.

Vice-President Breneman in the chair.

The minutes of the precoding meeting were read and approved.

Mr. L. E. M. del Monté was unanimously elected a member of the Society.

A paper was read by Prof. A. A. Breneman "On the Fixation of Atmospheric Nitrogen." Discussion followed.

The meeting was then adjourned.

D. WOODMAN,  
Recording Secretary.

## THE FIXATION OF ATMOSPHERIC NITROGEN.

By A. A. BRENEMAN, S. B.\*

### INTRODUCTION.

The great industrial problem indicated in the title of this article has been before chemists for half a century. It is doubtful whether there has been any real progress towards its solution since the ending of the first attempts to manufacture cyanides commercially and economically made by Possoz and Boissiere, at Newcastle-upon-Tyne, in 1844-1847. It would seem that the development of chemical theory within the same period should have thrown some light upon the more obscure points of the process, and the author has attempted in the following pages to define the present aspect of the problem, theoretically as well as practically. That the treatment is inadequate to the greatness of the subject he is fully aware. The limitations of his own time have made a fuller inquiry impossible at present. He can only hope that others may be led to follow up the subject more thoroughly. There is room for further experiment in this direction, both in the laboratory and on a large scale. The fixation of atmospheric nitrogen is an industrial problem to be compared with that involved in the manufacture of ammonia soda or of water gas, each of which passed through quite as discouraging an experience before attaining success as has, so far, been the lot of the nitrogen question. The question is still an open one, inviting further investigation. It has been taken up anew in recent years by Berthelot, from the theoretical side, and by Weldon from the industrial or practical side, and there is nothing in theory or practice at present to warrant the assumption that it is a hopeless question; in commercial importance it outranks either of the processes mentioned.

The matter given herewith relates principally to the preparation of cyanogen. The question of the synthesis of ammonia has been put somewhat in the background for lack of time and space. It is evident, however, that the fixation of atmospheric nitrogen in any one form is the solution of the general problem.

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\*The substance of this article was prepared as an appendix to a commercial report, but has not been printed heretofore in any scientific journal.—A. A. B.

# PART I.

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## HISTORICAL SUMMARY.

SHOWING THE PROGRESS AND DEVELOPMENT OF PROCESSES FOR  
THE MANUFACTURE OF CYANOGEN AND ITS DERIVATIVES.

### PRUSSIAN BLUE.

The familiar coloring matter, prussian blue, was discovered about 1710, but the chemical substance cyanogen, the radical common to prussian blue and to a large series of complex substances now known to chemistry, was not isolated until more than a hundred years later. The name cyanogen (generator of blue) was given by Gay Lussac, in 1814, to the new substance which he found to be the characteristic ingredient of this blue and of compounds related to it. The familiar name of "Prussiates," still applied in trade to the double cyanides of iron and potassium as well as the common name "Prussic Acid," by which hydrocyanic acid is known, bear evidence of the importance which the blue color originating in Prussia had early acquired as a commercial product.

Some time before the year 1710<sup>1</sup> a German manufacturer named Diesbach, working with the so-called Dippel's animal oil (commonly obtained by destructive distillation of bones, blood or other animal waste) happened, in handling a sample of this oil made from blood, to add to it a solution of potash (crude potassium carbonate) and obtained thereby a blue color. The process was soon applied upon a commercial scale. It was first described in a book called *Miscellanea Berolinensia*, published in 1710. But the discoverer of the color was not known by name until mentioned by Scheele in 1731.

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<sup>1</sup> Richardson—Watt's Chemical Technology, Vol. I., p. 1, *et seq.* (Referred to hereafter as R.W.)



Woodward & Brown, English chemists, each published a paper in 1724 upon the new blue. Woodward refers to a German from whom he had received directions for preparation of the blue, but gives no name.<sup>1</sup>

The process, as reported by Woodward, consisted in deflagrating a mixture of saltpetre and argols (crude potassium bitartrate) and fusing the product with dried blood. The resulting mass was lixiviated with water and the solution was treated with copperas and alum, producing a greenish precipitate which on heating with hydrochloric acid, yielded the blue color which has since been known as Prussian or Berlin blue. Brown (*loc. cit.*) substituted animal flesh for blood in the process. He also suggested that iron was essential to the color of the new substance.

Geoffry, in 1725, proposed the use of wool and charred horn instead of blood or flesh.

Scheele in 1731 published the name of Diesbach as the original discoverer. (R. W., *loc. cit.*)

In later modifications the use of nitre was abandoned and scrap iron was added to the mixture. The process as thus originated, is, in its essential features, that which exists to-day for the manufacture of potassium ferrocyanide from which prussian blue is made by precipitation with a ferric solution.

### Potassium Ferrocyanide.

Macquer (1750-60 ?) first made ordinary yellow prussiate of potash (potassium ferrocyanide) in the crystalline form by treating prussian blue with a concentrated solution of caustic potash.

Beaumé in 1773 proved the presence of iron in the same salt. The fact that iron was an essential ingredient of the salt remained for a long time unknown; as the proportion of iron varied in blue from different sources it was regarded as an impurity and many attempts were made to prepare a blue free from iron. Berthollet (1800-1806) determined the iron quantitatively.

<sup>1</sup> Phil. Trans., 1724. 33-34, 15-25. In the original edition of the Transactions, Woodward's article is in Latin and the name of Diesbach is not mentioned. In the later, uniform edition the article is in English and the name of Diesbach is given, in a foot note, as the German referred to.—B.

The researches of Gay Lussac, in 1814, first placed the composition of prussian blue and its related substances upon an intelligible basis by showing that they all contain the radical cyanogen, a compound of carbon and nitrogen (CN) which combines with hydrogen to form an acid and with metals to form simpler or complex cyanides of which latter prussian blue, ferric ferrocyanide,  $(\text{Fe}_4(\text{CN})_{12})$  is a good example.

This knowledge at once led to inquiries into the chemistry of the commercial manufacture of yellow prussiate of potash, a process which had previously been purely empirical.

The researches of Liebig led to the general theory at present accepted, namely, that potassium cyanide is the first product of the fusion of nitrogenous animal matters with potash and that the yellow prussiate found in the liquor after leaching the fused mass results from decomposition occurring between potassium cyanide and a compound of iron, generally ferrous sulphide, which is formed in the fused mass by action of metallic iron upon the sulphur of the animal matters. In proof of this view potassium cyanide can be extracted by alcohol from the fused mass previous to the addition of water.

Muspratt, in 1820 (loc. cit.) obtained by direct lixiviation of the fused mass, crystallized yellow prussiate which had been obtained previously, by the method of Macquer, from prussian blue.

Mackintosh in 1824 used closed pots for fusion and applied mechanical stirrers.

Gautier<sup>1</sup> suggested in 1827 and Gentile<sup>2</sup> in 1835 practically applied the use of raw animal matter instead of charring it before fusion with potash as had been done previously.

Naumann in 1837 allowed the flame to play directly upon the fused materials.

Up to this time the large loss of nitrogen during fusion and the small yield of ferrocyanide with respect to the theoretical yield (never more than one-third, generally much less) seems to have attracted comparatively little attention. But the increasing de-

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<sup>1</sup> J. de Pharm., 1827, 11.

<sup>2</sup> Dingl. pol. J. 129, 302.

mand for the prussiates in dyeing and the relatively greater cost of animal waste drew attention to the chemical problem involved in preventing this escape of nitrogen. It was found that the nitrogen was volatilized largely during fusion, as ammonia or organic bases, and the collection and utilization of these was attempted.

Kuhlmann in 1838<sup>1</sup> discovered that when ammonia was passed over red hot charcoal, cyanogen and ammonium cyanide were formed and by using a mixture of charcoal and potash for absorption he obtained potassium cyanide.

The idea of obtaining cyanides by passing ammonia over hot carbon, however, was probably of earlier origin.

Jaquemyn, applying this idea, passed the vapors from the prussiate pots over hot charcoal to obtain cyanides, and Berry<sup>2</sup> patented the same principle.

These facts relating to the conversion of ammonia into cyanides by the action of hot carbon are of interest as showing the development of chemical ideas upon the subject of cyanogen. They had their origin, however, mainly in the practical experience of the prussiate manufacture with its waste of nitrogenous vapors. Whatever interest they may have in connection with the history of the subject, they probably would not have led to the idea of atmospheric nitrogen as a source of cyanogen, except for another discovery originating also in an industrial process.

### Cyanogen from Atmospheric Nitrogen.

Zinken in 1813<sup>3</sup> had found a mass of fused salt mixed with carbonaceous matter in the lower part of a furnace at Rothehütte, which he partly examined and supposed to be principally chlorides. Koch (*loc. cit.*) found a similar mass at Königshütte in 1819. Berthier<sup>4</sup> also in 1826 remarked the presence of potassium carbonate as fused salt in the lower part of an iron furnace. No one seems to have tested these deposits or exudations for cyanogen until Dawes in 1835 announced the existence of potassium cyanide in them. No quantitative determination was made.

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<sup>1</sup> J. pr. Ch., 26, 410.

<sup>2</sup> Eng. Pat., Jan. 21, 1840. Jsb. chem. Tech., 1858, 184.

<sup>3</sup> J. pr. Ch., 26, 246. <sup>4</sup> Jsb. chem. Tech., 1829, 28.

In 1837 Neilson first introduced the use of the hot blast at the Clyde iron furnaces. Shortly afterwards,<sup>1</sup> a peculiar exudation of fused salt which hardened on reaching the air to a white, opaque mass was noticed upon the walls of the furnace near the boshes. The substance was regarded with much curiosity and it is related by Clark, who made the first analysis of the product, that its alkaline character was soon discovered by the workman and that it was used by the wife of one of them, for a time, as a substitute for soap in washing clothes.<sup>2</sup>

Clark's analysis showed it to contain potassium cyanide 43.4%, potassium carbonate 45.8%. No ferrocyanide was present. The mixture gave no blue color on addition of hydrochloric acid, but yielded a blue precipitate when ferrous sulphate (copperas) was added previous to the addition of the acid in excess. This furnace went on producing potassium cyanide for three years from this time.

Zinken and Bromeis<sup>3</sup> found in the bottom of a hot blast charcoal furnace at Madgdesprung in the Harz a carbonaceous mass containing iron and lead and a saline matter, which, on lixiviation, yielded the following potassium salts, namely, ferrocyanide, cyanide, carbonate, silicate and manganate. A similar substance was noticed by Redtenbacher (R. W., *loc. cit.*) in a hot blast furnace at Mariazell in Styria. Potassium cyanide was produced so abundantly in this case that it was sold commercially for galvanic gilding. The substance was found at the light hole, where the gases issue, and also in the pipes through which the gases pass from the furnace to the stoves.<sup>4</sup>

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<sup>1</sup> Probably produced more copiously in consequence of the action of the hot blast, as the circumstance had been only once reported before and has since been a common phenomenon of hot blast furnaces. Neilson had used the hot blast in iron furnaces as early as 1828, however. See "Bauerman's Metallurgy of Iron," p. 175.—B.

<sup>2</sup> *Pogg. Ann.*, 40, 815; *Dingl. pol. J.*, 65, 466.

<sup>3</sup> *J. Pr. Ch.*, 25, 246.

<sup>4</sup> I have, in my own experience, seen two cases of cyanide produced in blast furnaces. One from an anthracite furnace as an exudation from the wall below the boshes, the other from a furnace (at Irondale, West Va.), using coke, both, of course, hot blast furnaces. In the latter case no cyanides appeared upon the wall of the furnace, but a heavy, stony, grayish deposit formed in the downcast pipe through which the gases passed to the stove. It accumulated rapidly, forming a deposit like limestone in appearance, which threatened to clog the pipe and had to be broken away from time to time. Both samples were examined qualitatively, and found to be rich in cyanides. The gray color of the second sample was

Bunsen and Playfair<sup>1</sup> made an elaborate investigation of a furnace at Alfreton which yielded cyanides. The production of the substance was so abundant that it was estimated to amount to 224.7 lbs. in twenty-four hours. A hole was made in the front wall of the furnace, two feet nine inches above the tuyere or blast pipe, and the gases from that point were drawn off through a pipe for examination. Fumes of potassium cyanide escaped with the gases and condensed in the tube. Cyanides were obtained only from the lower part of the furnace; above the boshes none were found. These chemists believed that cyanides were produced only at a temperature corresponding to that at which potassium oxide gives up its oxygen to carbon. In the higher parts of the furnace cyanogen acts as a reducing agent and is destroyed by oxygen from the ores. When cyanides fall as low as the tuyere, on the other hand, they are burned, according to these authorities, by the blast of air. The conditions necessary for their production, therefore, are a reducing (deoxidizing) atmosphere or presence of hot carbon, and a temperature of the degree above mentioned.

Gases drawn from the furnace, as described above, had the following composition: Nitrogen 58.05%, Carbonic oxide 37.43%, Hydrogen 3.18%, Cyanogen 1.34%. These figures correspond to Nitrogen 79.2%, Oxygen 22.8% (instead of 20.08%; oxygen corresponding to water found in the gases is deducted). There is evidently here a deficiency of nitrogen as compared with ordinary air. At two feet above the tuyere no oxygen nor carbonic acid was found in the gases.

R. F. Smith<sup>2</sup> in 1865 found a compound oozing from the crevices of an old blast furnace at Kilmarnoch, which on analysis yielded 21.45% potassium cyanate, 47.73% potassium cyanide, 10.13% potassium carbonate.

A. v. Kirpely<sup>3</sup> describes the escape of a quantity of fused salts, chlorides and cyanides, from the slag hole of the blast furnace of Alsó Sajó in Hungary, just before the escape of the slag.

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probably, due to coke dust. The mass was probably formed from spray or vapor of fused potassium cyanide which, passing out of the furnace, condensed and solidified upon the wall of the pipe where it first became chilled, binding together, as it hardened, the furnace dust which accompanied it.—B.

<sup>1</sup> Report of British Association, 1845.

<sup>2</sup> Chem. News, 1865, Jsb. chem. Tech., 11, 54.

<sup>3</sup> Jsb. chem. Tech., 1879, 44.

The facts just given had an important influence upon chemical thought. The source of the large quantities of nitrogen combined in the cyanides thus obtained became a subject of active discussion. It was not at once admitted that the free nitrogen of the air could be taken into combination with carbon to form cyanogen under the conditions existing in the blast furnace. The tendency was, at first, rather to find the source of nitrogen in the fuel or in the ammonia of the air. But the answer was given in a series of accurate experiments which left no room for doubt, and the direct fixation of atmospheric nitrogen by hot carbon under given conditions has long been accepted as a fact in chemistry.<sup>1</sup>

The paper of Bunsen and Playfair was read before the British Association in 1845, but to take up the discussion methodically we must go back a few years. As has been said, the production of cyanides in the blast furnace at once raised the question of the source of the combined nitrogen, and the problem suggested by the furnace was soon transferred to the chemical laboratory.

Lewis Thomson, of Newcastle-upon-Tyne, in 1839<sup>2</sup> first proved that potassium cyanide is produced when coke, potash and iron filings are heated to a high red heat in contact with air, and he received the medal of the Society of Arts for his discovery. Priority is claimed for Defosses, who made a similar discovery about the same time at Besancon in France.

Fownes and Young<sup>3</sup> also confirmed these statements in 1841, using carbon prepared from cane sugar and pure potash.

Erdmann & Marchand, however, in 1842<sup>4</sup> repeated Fownes' experiments and reported that the process was uncertain and required very exact regulation of conditions to produce any cyanides at all. They concluded that no cyanogen is produced when the materials are perfectly dry.

Berzelius<sup>5</sup> remarked that these results of E. & M. agreed with the earlier results of Wöhler, in that water was shown to be necessary

<sup>1</sup> The experiments of Bunsen and Playfair showed also that, on the small scale and with a very slow current of nitrogen, *all* of the nitrogen was absorbed by the hot mixture of potash and carbon. It is much to be regretted that no record of the composition of the escaping gases was made in the commercial manufacture of cyanides by Possoz & Boisselerc.—B.

<sup>2</sup> *Dingl. pol. J.* 73, 281.

<sup>3</sup> *J. pr. Ch.*, 26, 407.

<sup>4</sup> *J. pr. Ch.*, 26, 412.

<sup>5</sup> *Jsb. d. fortschr. d. Chem.*, 1844, 23.

to the reaction. It was suggested that water plays the part of an intermediary in the reaction, first forming ammonia which is then converted into cyanide.

Langlois<sup>1</sup> discussed the question raised by Erdmann and Marchand. He made two experiments. 1. Moist, purified air was passed over a mixture of pure carbon and potash heated to high redness. Cyanogen was obtained. 2. Dry air under the same conditions also yielded cyanogen. The production of cyanogen in each case was tested by converting it into prussian blue in the solution obtained from the fused mass of carbon and potash. He found, however, that if a lead-glazed earthen tube were used instead of a porcelain tube, no cyanogen was obtained—lead in the glaze apparently decomposing cyanogen—and he ascribes the errors of Erdmann and Marchand to this fact.

Bunsen and Playfair<sup>2</sup> also attacked this question in their investigation above quoted. They passed nitrogen over a mixture of pure carbon and potash heated to high redness in a tube and obtained potassium cyanide. As the nitrogen was free from ammonia and the materials were chemically pure the origin of the nitrogen in the cyanide was placed beyond doubt.

Rieken<sup>3</sup> by very careful experiments confirmed the conclusion of Bunsen and Playfair as to the formation of cyanogen from pure carbon and nitrogen at a high temperature. He obtained pure carbon by heating pure cane sugar and pure potash by igniting pure crystallized potassium bicarbonate. The mixture of carbon and potash was then put into a tube and heated to whiteness, and nitrogen, prepared from air, was passed over it. This nitrogen was prepared by passing air through strong sulphuric acid and then through calcium chloride—thus removing both ammonia and water—then over iron filings heated white hot in a gunbarrel and finally through the mixture of white hot potash and charcoal. The highest white heat was required and the previous heating of the nitrogen was found to be essential. When the temperature was below whiteness no trace of potassium cyanide was formed.

Delbrück<sup>4</sup> added further to the weight of evidence in favor of

<sup>1</sup> Ann. ch. phys. [3] 1, 117.

<sup>2</sup> B. A. Rep., 1845.

<sup>3</sup> Dingl. pol. J., 121, 286.

<sup>4</sup> Jah. Chem., 1, 473.

the conclusion of Bunsen and Playfair. He showed that the direct union of carbon and nitrogen was incontestable and extended the limits of existing knowledge upon the subject by describing other related reactions in which cyanogen is formed. Nitric oxide and "potassium carbonic oxide"<sup>1</sup> were shown to produce cyanogen when heated. Carbon dioxide ( $\text{CO}_2$ ) mixed with ammonia, or even with nitrogen, when passed over hot metallic potassium, or ammonium carbonate kept in contact with fused potassium, also yielded cyanogen.

The fact of the direct union of nitrogen and carbon being settled and the practicability of carrying out the reaction on a commercial scale having been, in a certain sense, proven by the accidental phenomena of the blast furnace, attempts were made to build up a new manufacture, in which cyanides should be made direct from the nitrogen of the air.

The first patent taken out in England for manufacture of cyanides on the new principle was by A. V. Newton<sup>2</sup>. A patent taken out in 1839 by John Swindells<sup>3</sup> for the manufacture of cyanide might have come partly under the same head, as it involved the fusion of potassium or sodium sulphate, coal and iron in a reverberatory furnace. A portion of the nitrogen of the fire gases might have been taken into combination under these conditions as an alkaline carbonate is formed, but the process avowedly looked only to fixing the nitrogen of the coal as cyanide.

The specification of Newton especially prescribes that nitrogen from any source, but free from "oxidating substances" be forced through a layer of small pieces of charcoal saturated with "potashes" and heated to redness, the vapors containing cyanides to be absorbed by suitable liquids. He states that oxygen decomposes the cyanides at high temperatures; the necessity of excluding oxygen has always been recognized by other writers upon the subject as an essential feature of the process.

Newton used either charcoal, coal or coke, but preferred the former, in pieces the size of a hazelnut. The charcoal was satu-

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<sup>1</sup> The compound of the potassium retort (?)—B.

<sup>2</sup> Dingl. pol. J., 95, 293. Eng. Pat. No. 9965, Dec. 13, 1843.

<sup>3</sup> Eng. Pat. No. 8086.



rated with a strong solution of potash and dried before being put into the retort. A definite, maximum proportion of alkali was used; an excess prevents complete absorption of nitrogen and a deficiency involves loss (of carbon?). Twenty-five to one hundred parts of potash are used to one hundred of coal, according to the density of the latter. Nitrogen should always be in excess, but must not be passed too rapidly. A certain pressure upon the gas and much friction with the solids through which it passes are favoring conditions.

Newton recommends the use of waste gases from the sulphuric acid chambers after passing through ferrous sulphate and lime-water, to remove oxides of nitrogen. The use of these chamber gases has also been suggested by Binks, Firman and others.<sup>1</sup>

Before the date of Newton's patent, however, Possoz and Boissiere<sup>2</sup> had been at work upon the same industrial problem in France and had in operation at Grenelle, near Paris, in 1843, a small plant which was turning out yellow prussiate at the rate of 15,000 kilos, or more than fifteen tons per annum. The high price of fuel and the need of a cheap and abundant supply of highly refractory clay for making the retorts used in the process led them to remove, in 1844, to Newcastle-upon-Tyne, England, where they went into the operation on a large scale, under the patronage and coöperation of Bramwell and Hughes. The works here, in 1845, turned out yellow prussiate at the rate of more than a ton a day. They were run until 1847, and were then abandoned after considerable loss. The salt was said to be produced at the rate of less than two francs per kilo, and was of exceptionally fine quality.

This is the most persistent attempt on record to establish commercially a process for the fixation of atmospheric nitrogen, and as such deserves close consideration.

The process consisted of passing the gas from a coal fire through large vertical cylinders or retorts of fire clay filled with a mixture of wood charcoal and potash. The charcoal was prepared by saturating it with a solution of potash and then drying. Much

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<sup>1</sup> R. W., Vol. I. Pt. V. 61-65.

<sup>2</sup> *Jeb. chem. Tech.*, 1855, 83; 1858, 191. *Dingl. pol. J.*, 104, 446; 107, 444; 129, 361; 149, 56.

stress was laid by P. and B. upon exclusion of water in the process. The retorts were kept at the highest possible temperature—a white heat being preferred—as the rate of conversion of potash into cyanide was found to be proportional to temperature. The conversion was commonly completed after ten hours, but 2—3 hours in some cases was sufficient, with a good white heat. The cyanized charcoal was withdrawn at the bottom of the cylinder and dropped into a tank of water containing powdered spathic iron ore in suspension, by which the cyanides were converted into ferrocyanides or prussiates. The solution was finally filtered and evaporated to crystallization. The apparatus worked continuously<sup>1</sup>.

In the French experiments the retorts were seven to eight feet long with walls 2—3 inches thick. In England, much larger and heavier retorts were used. The high temperature, in connection with the alkalis, caused rapid destruction to the retorts. They were heated white hot before the introduction of the alkalized coal. White hot flues also served to superheat the nitrogen or furnace gases before entering the retorts. In later forms of the apparatus air was admitted directly to the cylinders, oxygen being removed in passing through the upper layers of carbon. The presence of carbonic oxide or carbon dioxide, as in the fire gases, was found to be disadvantageous. Coke yielded less cyanogen than charcoal. The production of cyanide was said to be greater for a given weight of potash than by the old prussiate process. The alkalized charcoal contained 30% of potash. Soda was found inferior to potash and required a higher temperature. Water, even in small quantities, hindered the production of cyanogen. This fact was ascribed by P. and B. to decomposition of the latter by water to form ammonia.

In the latest constructions the cylinders were 10 feet in length and 2 feet in diameter with walls 9 inches in thickness. These were built of fire brick and their massive character enabled them to retain heat and to resist wear so as to last several months in use. Lateral slits were also made in the walls of the cylinders for admission of air direct, and through these slits the contents could be

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<sup>1</sup>A cut of P. & B.'s furnace is given in R. W.; p. 68.

stirred to prevent clogging by fused potash which had been one of the chief obstacles in the process. The current of gas was upward and the charcoal was fed in at the top in moist condition and dried thus by waste heat. A pump drew the gasses through the cylinders.

The causes of failure assigned in England were the rapid destruction of apparatus owing to corrosion of the retorts by the alkali, and the great loss of alkali by volatilization, or absorption by the cylinders. Much potash was wasted in the fine charcoal after lixiviation or converted into silicates and other salts useless for further application in the process. Bramwell<sup>1</sup> patented some of the later improvements of P. & B.'s plant which were devised by him (Eng. Pat., Oct. 8, 1846). He preferred to convert oxygen of the air into carbonic acid rather than carbonic oxide before carrying it into the cylinders. The use of lateral slits is also a feature of his patents.

This process is said also to have been applied at several places in France, but was ultimately abandoned.

R. Laming, in 1843,<sup>2</sup> patented a process for manufacture of hydrocyanic acid by passing ammonia through red hot charcoal.

Swindell, in 1844,<sup>3</sup> patented a process in which nitrogen or air or oxides of nitrogen were passed through charcoal or other carbonaceous material, heated to full redness in a perfectly close retort. If ammonia is to be formed, steam is mixed with the nitrogenous gas.

J. Laming obtained a patent in 1845,<sup>4</sup> (for another party), by which charcoal or other form of carbon in powder is mixed with alkali and the mixture is kept in fusion while a current of ammonia is passed through it for the production of cyanides.

Bunsen<sup>5</sup> proposed the construction of a furnace for the production of cyanides on the plan of the blast furnace. It was to be charged with alternate layers of coal and alkali and the fused cyanide was to be drawn off periodically at the bottom (p. 8). No industrial application of this idea is known, although Binks is

<sup>1</sup> Dingl. pol. J., 104, 446.

<sup>2</sup> Eng. Pat., No. 9832, July 13, 1843.

<sup>3</sup> Eng. Pat., June 12, 1844.

<sup>4</sup> Eng. Pat., No. 10955, Nov. 18, 1845.

<sup>5</sup> Rep. Brit. Assoc., 1845.

said (R. W., p. 66), to have taken out a patent for a similar furnace.

Armengaud patented in France, in 1846, a furnace for manufacture of cyanides from the nitrogen of the air.<sup>1</sup> Unlike P. & B. he regards the presence of steam as favorable to the process and prescribes its regular admission to the furnace. The charcoal, which must be in excess, is intimately mixed with potash, soda or lime, the mass is heated to a cherry red and over it is passed a mixture of furnace gases and steam. The absorption chamber resembles a reverberatory furnace. The product is leached with water at 75–85°C. The volatile products from the furnace are carried into a solution of ferrous sulphate.

F. Ertel in 1846 took out a French patent for a process very similar in principle to the above,<sup>2</sup> involving the use of steam, or better as the inventor says, of hydrogen. Air from a coal fire is passed through a column of coal or coke heated to a cherry red and from this through a mixture of charcoal powder and alkaline carbonates or lime, also heated to cherry red. The distinctive features of Armengaud's and Ertel's process are the use of steam and the application of a comparatively low temperature, whereas Possoz and Boissiere insisted upon a white heat and the exclusion of steam, as essential conditions.

The history of later attempts to utilize the nitrogen of the air for the manufacture of cyanides, shows, up to the present time, no commercial success. The few further plans or suggestions bearing upon the question are added here as having a possible bearing upon the future study of it.

Margueritte and Sourdeval in 1862<sup>3</sup> found that when air is passed over a hot mixture of baryta and carbon, nitrogen is absorbed freely, forming barium cyanide, and that this compound in presence of steam at 300°C. yields ammonia. In another form of the process they passed a mixture of illuminating gas and nitrogen over a mixture of coal and barium carbonate. The resulting barium cyanide was decomposed in solution by potassium sulphate.

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<sup>1</sup> *Dingl. pol. J.*, 120, 111 (with diagram): *Genie Industriel*, 1853, 315.

<sup>2</sup> *Dingl. pol. J.*, 120, 77: *French Pat.*, Nov. 16, 1846.

<sup>3</sup> *Jeb., chem. Tech.*, 1873, 361: *Ber.* 1873, 79.

They also used iron filings in one of their methods similar in other respects to the foregoing. This process, which seemed to promise much for the industrial uses of nitrogen, has never received any commercial application, even as a source of ammonia<sup>1</sup>. English patents for the process were taken out by Clark.

Diess in 1873<sup>2</sup> patented in France a method for the manufacture of cyanides which differs in no essential feature from that of Possaz and Boissiere (p. 12).

S. Q. and A. Brin, in 1883,<sup>3</sup> patented a process for manufacture of ammonia by passing moist nitrogen over coke containing baryta, which recalls that of M. and S. They also utilized oxygen separated from the air by another process.

Berthelot,<sup>4</sup> in 1868, made a valuable contribution to the theory of the synthesis of cyanogen. He obtains acetylene ( $C_2H_2$ ) by direct combination of its elements (under the influence of the electric spark) and converts this in presence of nitrogen by the same means into hydrocyanic acid ( $HCN$ ). He says that when nitrogen acts upon a highly heated mixture of nitrogen and potash, the compound potassium acetylene ( $C_2K_2$ ) is first formed and that this, by direct union with nitrogen, forms two molecules of potassium cyanide ( $KCN$ ). ✦

J. Blair,<sup>5</sup> in 1878, patented an apparatus in the United States for manufacture of cyanides. Gases from a coal fire (a stack with a deep layer of coal) are drawn over a layer of heated iron ore to form carbonic acid by oxidation of the carbonic oxide. The former is absorbed by passing the gases through milk of lime, and the resulting nitrogen is carried to a holder. The nitrogen is then carried upwards through a hot mixture of potash and charcoal in a stack heated externally by a fire in a larger stack which encloses it. The charcoal is drawn from the bottom and leached. Fumes of potassium cyanide which escape from the stack are condensed in a chamber adjoining and the lighter fumes are absorbed by a solution of a salt of iron.

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<sup>1</sup> Comptes Rend., 50, 1100; Dingl. pol. J. 187, 73, 337.

<sup>2</sup> E. Meyer, Jah. chem. Tech., 1874—442.

<sup>3</sup> Eng. Pat. No. 5802, Dec. 18, 1883.

<sup>4</sup> Jah. chem. Tech., 1869, 300; Comptes Rend., 67, 1141; J. pr. Ch., 107, 272.

<sup>5</sup> Scientific American, 1878, 21 (with cut), Dingl.; pol. J., 230, 93.

Walter Weldon, in 1879,<sup>1</sup> obtained a patent in England for the manufacture of cyanides. He finds that the temperature necessary for absorption of nitrogen by alkaline charcoal is not so high as has been supposed.<sup>2</sup> Instead of a white heat, Weldon finds that a comparatively low temperature, a bright red or even a lower heat, suffices to produce cyanides from mixtures of alkalis or alkaline earths with carbon in presence of air. His apparatus consists of a rotary furnace similiar to that used in preparation of black ash (soda ash).

V. Alder, in 1881<sup>3</sup>, brought forward a method involving some new features. Oxides, hydrates or carbonates of the alkalis or alkaline earths with charcoal are used to absorb nitrogen prepared by passing air or fire gases through solutions of potassium or barium sulphide or by passing air over iron, copper or zinc. He asserts that presence of finely divided metallic iron is useful in the process<sup>4</sup> and supplies this by saturating charcoal or coke with a solution of ferrous sulphate and then igniting it in a current of hydrogen. Sulphates and sulphides of the alkalis are also used, together with lime, in place of other alkaline bodies above mentioned. In a later patent (D. R. Pat., No. 18, 945, 1881) the admixture of hydrocarbon gases or carbonic oxide with the nitrogen is recommended; also the fuel in fragments is coated with a pasty mass made by mixing a strong solution of a soluble salt with charcoal powder, sawdust, etc. These modifications are introduced with the object of increasing the surface available for absorption of nitrogen.

Ludwig Mond, in 1882<sup>5</sup>, obtained a patent for manufacture of cyanides and ammonia by calcining, out of contact with air, a mixture of carbon, barium carbonate, or oxide, and magnesia, previously

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<sup>1</sup> *Jeb. chem. Tech.*, 1879, 472.

<sup>2</sup> Armengaud and Ertel (p. 30) both advocated the use of moderate temperatures—cherry red—and Margueritte and Sourdeval showed that baryta in presence of charcoal absorbed nitrogen at a comparatively low temperature, and that a light red or even a lower temperature is sufficient.

<sup>3</sup> *Jeb. chem. Tech.*, 1881, D. R. Pat. 12,851. 1882, 509.

<sup>4</sup> This was suggested by L. Thomson in 1839. It would naturally occur to any one familiar with the old prussiate process, but the conditions are different in the two cases and the reason for using it here is not apparent. The carbide of iron may possibly play an intermediate part in the production of cyanogen, such as Berthelot supposes to be played by  $C_2K_2$ , as above quoted.—B.

<sup>5</sup> U. S. Pat. 292,209, Dec. 19, 1882.

compressed into blocks, and then exposing these heated blocks to a current of nitrogen. In an improvement he first heats the nitrogenous gas by passing it through hot barium salts and then passes it through fresh layers of barium salts and carbon at the temperature required for forming cyanogen compounds.

Fogarty, in 1883,<sup>1</sup> took out two patents in the United States for production of cyanides and ammonia, which consisted essentially in dropping a mixture of powdered carbon and alkali into superheated furnace gases or superheated "generator gas" (a mixture of nitrogen, hydrogen, carbon dioxide, carbon monoxide, and steam), whereby cyanides were produced, which were subsequently decomposed by steam, yielding ammonia. He also obtained two similar patents in 1887<sup>2</sup>. In one of these processes the mixture of superheated furnace gases or generator gas is mixed with steam in excess, with the object, as explained by the author, of first producing cyanides and cyanates, and then, in the same mixture, decomposing these by the steam present to produce ammonia.

In the second of these patents both air and steam are in excess. Cyanides are supposed to be produced, and subsequently decomposed by the excess of steam to produce ammonia. The latter in presence of carbonic acid of the mixed gases is supposed to form ammonium carbonate, and this is said to be decomposed by gypsum, yielding calcium carbonate and ammonium sulphate. These processes have been tried on a large scale experimentally, but are not as yet commercially successful.

J. Young, in 1884<sup>3</sup>, patented a process for cyanides intended to meet the difficulty hitherto encountered in the rapid destruction of the apparatus. He proposed to use magnesian lime stone or other suitable basic substance for constructing the retorts.

Siepermann<sup>4</sup> (1887) obtains cyanates by passing ammonia over a mixture of barium carbonate with alkaline carbonates. For cyanides he adds coal powder to the mixture. He gives the results of experiments, showing the effect of temperature upon the production of cyanides. Excessively high temperatures yielded poorer results than a moderate red heat.

<sup>1</sup> U. S. Pat. 298,323 and 402,324, Nov. 13, 1883.

<sup>2</sup> U. S. Pat. 371,186, and 371,187, Oct. 11, 1887.

<sup>3</sup> *Jab. chem. Tech.*, 1887, 675.

<sup>4</sup> *Eng. Pat. No. 16046*, Dec. 6, 1884.

Dickson in 1887,<sup>1</sup> patented a process for production of cyanides and ammonia by injection of a mixture of air, steam, coal dust or hydrocarbon vapor, and powder of alkalies or alkaline earths, into a chamber heated by the combustion of the injected, finely divided fuel alone. His method also contemplates the maintaining of pressure (one to three atmospheres) in the furnace.

### The Formation of Metallic Nitrides.

R. Wagner in 1857<sup>2</sup> had suggested that nitrides of boron and silicon in the interior of the earth might be the source of the ammonia found in combination with boric acid in the lagoons of Tuscany and as sal ammoniac in volcanic exhalations. This ammonia may be a product of the action of water at high temperatures upon the above nitrides. Bunsen, however, and Rainer, (*loc. cit.*) regard volcanic ammonia as of organic origin, resulting from action of subterranean heat upon fossil vegetable matter, coal, lignite, etc.

Briegleb and Geuther in 1862<sup>3</sup> investigated the question of the metallic nitrides. The close relation of these bodies to the cyanides renders a knowledge of them of much interest in this connection. Nitrides of magnesium, aluminium and chromium were obtained by simply heating the metals in pure nitrogen. The temperature of combination of nitrogen with the metal seems to be near the melting point of the latter. Magnesium nitride is a greenish yellow, amorphous mass which yields ammonia in contact with water or caustic alkalies, and yields cyanogen when heated in an atmosphere of carbonic oxide, or carbon dioxide. It has the composition  $Mg_3N_2$ .

Tessie de Motay in 1872<sup>4</sup> announced that titanium nitride could be made to yield ammonia by the action of steam and could then be regenerated by submitting it to a current of nitrogen and the action thus alternated successively.

Mallet in 1876<sup>5</sup> obtained magnesium nitride by the combustion of

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<sup>1</sup> U. S. Pat. No. 370,768, Oct. 4, 1887.

<sup>2</sup> *Jab. chem. Tech.*, 1857, 121.

<sup>3</sup> *J. pr. Ch.* 123, 228.

<sup>4</sup> *Jab. chem. Tech.*, 1873, 379; *Ber.*, 1872, 395.

<sup>5</sup> *Proc. Am. Chem. Soc.*, 1, 17.



magnesium powder in a crucible with insufficient admission of air. Other nitrides, of boron, titanium, silicium, etc., have been investigated by Ufer, Uhrlaub, Wohler, Deville and Caron.<sup>1</sup>

### Cyanogen from Oxides of Nitrogen.

Binks<sup>2</sup> proposed to use oxides of nitrogen or vapor of nitric acid for production of cyanides. The gases were brought in contact with vapors of hydrocarbons in passing through a highly heated cylinder filled with firebrick. When the nitrogen compounds are in excess ammonia is chiefly produced, but with hydrocarbons in excess cyanides are the principal products. Crane and Jullion (*loc. cit.*) used a somewhat similiar process, using, however, an excess of water gas (hydrogen and carbonic oxide) mixed with the oxides of nitrogen and hydrocarbon vapors, and passing the mixture over a hot catalytic substance (platinized asbestos) at a temperature of 600° F.

Firman (*loc. cit.*, p. 65) and others have proposed the use of waste gases of the sulphuric acid chamber (nitrogen, oxides of nitrogen, etc.) for the same purpose.

A process suggested by Roussin in 1858<sup>3</sup> uses oxides of nitrogen in a different way and recalls the very early methods of Diesbach and Woodward (p. 4). With the object of converting nitrates into cyanides he made the following experiment: Four equivalents of crude potassium acetate were mixed with three of potassium nitrate (nitre) and five of potassium hydrate or carbonate, and heated in a porcelain crucible to 350° C. The mass burned briskly leaving a black residue which, on lixiviation, yielded potassium cyanide and carbonate. By addition of coal powder, to make up for the deficiency of carbon in the organic acid, an increased yield of cyanide was obtained, but still short of the theoretical result. Previous reductions of the nitrate to nitrite yielded better results, and a mixture of potassium acetate and nitrite with lampblack gave 2.6 parts of Berlin blue (dried at 100° C.) to 13 parts of acetate, and an ammoniacal odor during the operation showed a loss of nitro-

<sup>1</sup> J. pr. Ch., 101, 359; 103, 230; 105, 89; 110, 248.

<sup>2</sup> R. W., Vol. 1, Pt. V., p. 60. Eng. Pat. No. 10911, Nov. 3, 1845.

<sup>3</sup> Comptes Rend., 67, 875. J. pr. Ch., 78, 375.

gen. Potassium tartrate yielded little cyanide when used to replace the acetate, a fact already announced by Guibourd. Rousin suggested that a commercial process could be based on the use of crude sodium nitrate and acetate.

### Production of Cyanides from Ammonia.

The reactions by which ammonia is converted into cyanides are so closely related to the direct production of cyanides from nitrogen and offer so many points of suggestion in connection with the same, regarded as an industrial problem, that the history of them cannot be omitted from this summary.

The original experiment, ascribed by Langlois<sup>1</sup> to Scheele, of heating together sal ammoniac, potash and charcoal and obtaining potassium cyanide may be regarded as the starting point.

Liebig attributes to Scheele (1750-80 ?) the statement, that ammonia passed over hot charcoal yields hydrocyanic acid, but Langlois does not find this in Scheele's writings. What Scheele does say is that when sal ammoniac is heated with vegetable charcoal and potash the mass yielded on lixiviation "*la lessive du sang*."<sup>2</sup> (Langlois, loc. cit.)

Clouet in 1791<sup>3</sup> mentioned that ammonia gas passed over hot charcoal yields hydrocyanic acid. He states that Thenard had noticed that a soluble substance having the odor of bitter almonds was formed under the same conditions. Bonjour, Vauquelin, Buchholz, Schroder and Ittner<sup>4</sup> all refer to the same fact as based upon experiments in which ammonia or ammonium chloride was heated with charcoal or with mixtures of charcoal and lime or oxide of lead.

<sup>1</sup> Ann. ch. phys. [3] 1, 117.

<sup>2</sup> That is, potassium ferrocyanide, yellow prussiate of potash, called also in German "*blutlaugensalz*." The iron must have come from impurities in the materials. In the "Life of Scheele," given in Crell's Journal, Vol. I, p. 12, 1891, the author says: "His experiments on the coloring matter of Prussian blue, the methods of separating it, its properties and in short the discovery of its artificial composition from charcoal, fixed alkali and sal ammoniac, may be mentioned amongst the most valuable of the performances with which he has presented us." The biographer also refers to fuller accounts of this work in The New Transactions of the Royal Stockholm Academy, Vol. III, p. 256, and Vol. IV, p. 32. These sources of information are not accessible to me.—B.

<sup>3</sup> Ann. ch. phys., 11, 30; J. pr. Ch., 26, 408. Crell's Annalen 1796. This latter reference, which is probably the original source, I have not had access to.—B.

<sup>4</sup> J. pr. Ch. 26, 409.

The product was probably ammonium cyanide, as in later repetitions of similar experiments, but the constitution of the cyanides was not then understood as this was before the date of Gay Lussac's discovery (1814). Clouet reported that hydrocarbons, carbonic acid and nitrogen were set free at the same time, while Bonjour showed that hydrogen was the only by-product, an observation that was fully confirmed by Langlois in 1841. Trommsdorf,<sup>1</sup> however, was first to recognize ammonium cyanide in the products of this experiment.

Kuhlmann<sup>2</sup> found that volatile nitrogen compounds containing all hydrogen or mixed with volatile hydrocarbons, when passed together with carbonic oxide over hot platinum sponge, yielded ammonia. He refers to Clouet's experiment, and shows, by a repetition of the same, that no hydrocyanic acid, but only ammonium cyanide, is produced. Marsh gas ( $\text{CH}_4$ ) is separated at the same time. He regards the process of preparing alkaline cyanides as involving first the formation of ammonia, which, in presence of alkali and excess of carbon, is converted into cyanogen and carbonic oxide. Langlois<sup>3</sup> repeated Scheele's experiment with sal ammoniac, but obtained no cyanide. He also obtained ammonium cyanide by passing ammonia over hot charcoal, and called attention to the remarkable way in which ammonium cyanide resists decomposition at high temperatures.

The processes of Jacquemyn and Berry in this direction have already been mentioned (p. 6).

Graeger<sup>4</sup> passed vapor of ammonium carbonate through alkaline charcoal contained in narrow iron cylinders  $1\frac{1}{2}$  inches in diameter, and obtained 93 to 95% of the theoretical yield of ferrocyanide. When large and wide cylinders were used the results were much inferior, only 15 to 30% being obtained.

Brunquill,<sup>5</sup> in 1856, proposed to apply the same principle to the production of cyanides and prussiates. Ammonia, or the vapors from distillation of bones, etc., are passed over hot firebrick

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<sup>1</sup> Ibid.

<sup>2</sup> Ibid. Ann. Chem. (Liebig), 38, 62: J. pr. Ch., 16, 482.

<sup>3</sup> Ann. ch. phys. [3], 1, 117.

<sup>4</sup> Jsb. chem. Tech., 1858, 184.

<sup>5</sup> Preuss. Verhandlungen, 1856, 30. Jsb. chem. Tech., 1856, 102. Dingl. pol. J., 140, 374, 452.

and then over hot wood charcoal in pieces of the size of a chestnut. The volatile ammonium cyanide is absorbed by solution of ferrous sulphate in an apparatus of peculiar construction. A portion of the ammonia is recovered as sulphate, and used anew in the process. The precipitated cyanides of iron are converted by potash or soda into prussiates. The advantages of this method are the prevention of waste of potash and of nitrogen. Only moderate temperatures being employed, there is no loss of potash by volatilization, by absorption, or by formation of unavailable salts of potash, all of which occur in the old process. The cost of the ammonia is defrayed by the increased value of the residue when bones are used. The author hoped also to obtain ammonia for the first stage of the process by passing air and steam over coal.

Levoir, in 1859,<sup>1</sup> noticed that a flame of ammoniacal gas yielded cyanogen (ammonium cyanide) in burning. Fischer<sup>2</sup> questioned this statement, saying that he had repeated Levoir's experiment with an argand burner, and obtained no cyanogen. The fact was verified, however, a few years later by Romily.

H. Johnson,<sup>3</sup> in 1860, obtained in England a patent for a method, devised by J. V. Lucas in Paris, for preparation of prussiates, which consists simply in saturating wood charcoal with potash solution, drying and heating it to redness in a retort, and passing ammonia over it. The charcoal is mixed also with 5% of iron filings.

J. Webster, in 1860,<sup>4</sup> patented in England a process for manufacture of prussiates by charring or burning a mixture of sawdust or spent bark and oxide of iron, charging the mixture with potash and passing ammonia through it.

Fleck,<sup>5</sup> in 1863, proposed to make cyanides as follows: A hot mixture of charcoal or coal, sulphur and potash is treated with a definite quantity of ammonium sulphate. Potassium sulphocyanate is formed. Ammonia in part escapes, but is absorbed and utilized. The sulphocyanate is decomposed by metallic iron, yielding

<sup>1</sup> J. Pr. Ch., 76, 447. Dingl. pol. J., 153, 466.

<sup>2</sup> Dingl. pol. J., 157, 466.

<sup>3</sup> Dingl. pol. J. 156, 312. Jsb. chem. Tech., 1860, 221. (with diagram).

<sup>4</sup> Eng. Pat., No. 1912, Aug. 8, 1860.

<sup>5</sup> Polyt. Centralbl., 1863, 717. Dingl. pol. J. 160, 200. Jsb. chem. Tech., 1863, 222.

potassium cyanide and ferrous sulphide. It was claimed by the author that 94.42% of the ammonium salts used were ultimately converted into cyanides. This process is referred to by Meyer ten years later, 1874, as not being successful in practice.

Gelis,<sup>1</sup> in 1862, manufactured prussiates in Paris after a new method of his own invention, for which a medal was awarded at the London Exhibition of 1862. It consists in mixing, in the cold, a solution of ammonium sulphhydrate ( $\text{N H}_4 \text{ H S}$ ), obtained from gas liquor, with carbon disulphide; ammonium sulphocarbonate ( $\text{NH}_4)_2\text{SCS}_2$ ) is formed and sulphuretted hydrogen. The addition of potassium sulphide to the sulphocarbonate results in the production of potassium sulphocyanate, which by action of iron can be converted into cyanide or prussiate. The by-products, ammonium sulphate and sulphuretted hydrogen, are again used. The process is carried on in a retort and these products are readily recovered. The cost by this process was said by Payen to be within 1.6 francs per kilo (about 15 cts. per lb.) for potassium ferrocyanide.

Meyer, in 1874 (p. 25), remarks that the conversion of potassium sulphocyanate into cyanide by iron is wasteful of nitrogen when fusion is resorted to and incomplete in the cold. The process of Gelis was finally abandoned.

Romily,<sup>2</sup> in 1867, repeated the experiment of Levoir (p. 27), and improved upon it. Illuminating gas was made to bubble through ammonia and then burned from a jet, and the flame was made to impinge upon a surface of water containing caustic potash in solution. Potassium cyanide was found after a time in the solution. Solutions of sodium and calcium hydrates gave corresponding results. When distilled water was used ammonium cyanide was found in the liquid. The effect was produced only when the flame was luminous or smoky; the flame of a Bunsen lamp yielded no cyanides. Vapors of oils or hydrocarbon gases containing ammonia gave similar results. Vapor of water in the mixture of gases did not prevent the formation of cyanides. When iron in fine powder

<sup>1</sup> *Annales du Conservatoire des Arts et Metiers*, 1862, 37. *Jab. chem. Tech.*, 1862, 283.

<sup>2</sup> *Compt. Rend.* 64, 320; 65, 865. *Jab. chem. Tech.*, 1867, 761.

was suspended in the alkaline solution ferrocyanide was formed.<sup>1</sup>

An apparatus was devised to apply the principle industrially. A cylinder of iron revolving on a horizontal axis, dipped into a tank containing an alkaline solution. A pipe, parallel with the cylinder and pierced with holes, supplied ammoniacal illuminating gas, burning in a line of jets which impinged upon the face of the cylinder. The cyanides were absorbed by the film of alkaline liquid which was continually renewed as the cylinder revolved.

Schwarz,<sup>2</sup> in 1869, obtained ammonium cyanide by passing vapor of carbon disulphide mixed with ammonia over hot iron or copper in an iron tube. Sulphide of the metal is simultaneously formed. The vapors are passed into a mixture of solutions of caustic potash, ferrous sulphate and ferric chloride and the resulting mass is converted into Prussian blue by hydrochloric acid, and then by potash into yellow prussiate. Schwarz also confirmed the conclusions of Levoir and Romily (p. 23-24) as to the production of ammonium cyanide during the combustion of ammoniacal illuminating gas, and he suggests that the purification of such gas from ammonia is, on this account, a matter of the greatest importance.

Frohde remarks<sup>3</sup> that the fumes from burning coal may be noxious, not merely because of oxides of carbon in them, but also because of cyanogen. He claims to have detected cyanogen by its odor where coal was incompletely burned.

E. Meyer,<sup>4</sup> in 1874, published a review of the cyanogen industry up to the year of the Vienna Exhibition (1873). He found the old method still the only important one. The problem of making cyanides from nitrogen of the air was still unsolved, and the earlier efforts of Possoz and Boissiere (p. 12) had not been even equalled in its results by the later one of Margueritte and Sourdeval, from which much was at first expected. The methods using ammonia as a source of nitrogen for the manufacture of cyanides had not re-

<sup>1</sup> The discoveries of Levoir and Romily recall the early observations of Kuhlmann, who showed that ammonia and all volatile compounds of nitrogen yielded ammonium cyanide when mixed with hydrocarbons (or even with carbonic oxide in the case of ammonia), and passed over platinum sponge at a temperature of 600° F.—B.

<sup>2</sup> Bull. soc. chim., 1869, 167. Dingl. pol. J., 191, 399. Jsb. chem. Tech., 1869, 369.

<sup>3</sup> Watt's Dict. Supp., I., 537.

<sup>4</sup> Jsb. chem. Tech., 1874, 443.

placed the old method, through dry distillation of animal matters, (Karmrodt, and others)—which are treated by fusion in the old process—nor by substitution of ammonia salts as a source of nitrogen for these substances (Fleck, p. 23). Neither had the methods based upon formation of sulphocyanate (Gelis) marked any great success. The production of sulphocyanate is readily brought about by Gelis' method and the process is, so far, a success; but the conversion of this salt into cyanide or ferrocyanide is difficult. It does not stand sufficiently above the usual raw materials (animal matters) used for this purpose, in its proportion of nitrogen, to counterbalance the disadvantage which it offers in comparison with them from its high proportion of sulphur.

F. Maxwell-Lyte<sup>1</sup> patented, in 1875, a process for manufacture of ammonia by bringing nitrogen in contact with nascent hydrogen liberated in the presence of a triad or pentad element.

Tscherniak and Gunsberg,<sup>2</sup> in 1878, patented a method, in Germany,<sup>3</sup> for the manufacture of cyanides similar in principle to that of Schwarz (p. 25). Two parts of ammonia water of 85%, and one of carbon disulphide are put into a tight vessel, heated to 110° C. below and cooled above so that a continuous distillation of the volatile substances occurs. After three or four hours the mixture is found to be converted into ammonium sulphocyanate and sulphuretted hydrogen. The ammonium salt is converted into calcium sulphocyanate, which, by action of an alkaline sulphate or carbonate, yields the corresponding alkaline salt, and this, by heating with coal, lime and iron, yields cyanides or prussiates. The ammonia is recovered and used again.

Graham Young, in a process for the manufacture of ammonia patented in England in 1880, has suggested the use of electricity to effect the union of nitrogen and hydrogen. The principle had also been mentioned in an English patent issued to Chisholm and Kent in 1860. No practical result has as yet come from these suggestions.

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<sup>1</sup> U. S. Pat. 161,187, March 23, 1875.

<sup>2</sup> Ber., 1879, 140. Dingl. pol. J., 232, 80. *Jeb. chem. Tech.*, 1879, 471; 1882, 570.

<sup>3</sup> D. R. Pat. 3,199, April 9, 1878.

**The Decomposition of Alkaline Hydrates by Metals in Presence of Air to Produce Ammonia.**

Dufrenó<sup>1</sup>, in 1880, patented a process in England for the manufacture of ammonia by combustion of zinc in air, in presence of an alkaline hydrate. Hydrogen and nitrogen are both set free and combine to form ammonia under the influence of a porous solid, such as iron or platinum sponge in a heated state.

Twinch<sup>2</sup>, in 1881, proposed to manufacture ammonia by using oxide of nitrogen (nitric oxide ?—B.) to remove oxygen from air; the resulting nitrogen (which is said to be nascent and peculiarly active?—B.) is brought in contact with nascent hydrogen from the decomposition of steam or of alkaline hydrates by metals, to produce ammonia.

*(To be concluded.)*

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<sup>1</sup> Eng. Pat. No. 5478, Dec. 29th, 1880.

<sup>2</sup> Eng. Pat. No. 3712, Aug. 25th, 1881.





**REGULAR MEETING, Feb. 1st, 1889.**

**Vice-President BRENNEMAN in the chair.**

**The minutes of the previous meeting were read, amended and accepted.**

**The following new members were unanimously elected :**

**Mr. John A. Mandel, New York.**

**Dr. F. P. Vandenberg, University of Buffalo.**

**Harold H. Fries, Ph. D., 92 Reade street, New York.**

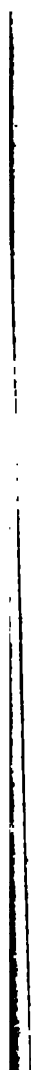
**DR. E. WALLER read a preliminary paper "On the Assay of Zinc Ores."**

**MORRIS LOEB, Ph. D., Newport, R. I., was nominated for membership:**

**The resignation of MR. J. F. KELLY was read and accepted.**

**The meeting was then adjourned.**

**DURAND WOODMAN, Rec. Sec'y.**



# THE FIXATION OF ATMOSPHERIC NITROGEN,

BY

A. A. BRENNEMAN, S. B.

(Concluded.)

## PART II.

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### AN INQUIRY IN REGARD TO THE CONDITIONS UNDER WHICH CYANOGEN IS PRODUCED BY DIRECT UNION OF NITROGEN AND CARBON.

The union of nitrogen with other chemical substances is brought about with so much difficulty that it has long been the custom to speak of nitrogen as an inert substance showing little affinity for or tendency to combine with other elements, yet the very large classes of compounds in which nitrogen is an essential element show that it is not difficult to retain it in a compound once formed, or to hand it over from one compound to another in the reactions by which chemical compounds are formed or decomposed. The difficulty then, is simply that of getting free nitrogen, as it exists in the air, to enter into direct combination with any other element, and this difficulty is so real and serious that, practically, all of the nitrogenous compounds used in the arts are obtained by the decomposition of other nitrogen compounds. Free nitrogen is one of the most abundant substances on the earth, and combined nitrogen is essential to some of the most valuable of commercial products, but the ready fixation of the nitrogen of the air on a manufacturing scale in any single compound which may be used as the starting point of a series of substances derived from it, has yet to be accomplished.

This indifference to combination together with the considerable degree of permanence given by nitrogen to the compounds into which it enters, lead to the conclusion that a certain quantity of work, represented by a certain quantity of heat, has to be done in order to bring free nitrogen to the condition in which combination is possible. The chemist explains this by saying that the condition of free nitrogen is that of two atoms joined to one another to form a molecule and requiring the expenditure of a certain quantity of heat to tear them apart and leave each atom free to enter into new combinations.

The most prominent source, perhaps the only true source, of nitrogenous compounds in nature is found in the union of nitrogen and oxygen of the air under the influence of the electric discharge as in lightning, etc. Nitric acid is washed down from the air by rain during a thunder storm, either free or as ammonium nitrate or nitrite, and these substances, and ammonia, the product of their reduction, are the starting points of mineral, vegetable and animal compounds containing nitrogen. The conversion of nitrogen of animal and vegetable matter into ammonia and nitric acid under the influence of bacterial life is a secondary process and does not deal with free nitrogen.

Whether the union under the influence of the electric spark be purely a heat effect, or whether it results in part from a special polarity impressed upon the atoms of nitrogen by the discharge, it is now definitely proven that heat alone in presence of a strongly basic substance, like an alkali, is sufficient to effect the combination of nitrogen and carbon. The discovery, made accidentally, that the hot blast iron furnace fulfils at times the conditions necessary for the production of cyanogen from nitrogen of the air, was the beginning of a series of experiments upon the fixation of free nitrogen which have cast much light upon the nature of the problem.

Nevertheless, the conditions of the blast furnace furnish the best basis for the study of the question, and most of the early attempts to fix atmospheric nitrogen as cyanogen have striven to imitate these conditions more or less closely. Bunsen indeed (p. 19) suggested the construction of a furnace on the plan of the blast furnace for production of cyanides only, but it is difficult to see the

practicability of such a plan unless the size of the furnace were very much reduced or the yield of cyanides very small as compared with consumption of fuel. We have to inquire then, what are the essential and what the non-essential conditions for the fixation of free nitrogen as cyanogen? The investigations of the blast furnace itself with this object has been done by Bunsen and Playfair (p. 13), and the various forms of apparatus which have been applied to the manufacture of cyanides upon this plan and the experience drawn from them furnish much additional material for such an inquiry.

We are limited here to the study of the synthesis of cyanogen, but the conversion of the nitrogen of the air into ammonia or cyanogen on the one hand, or into an oxide of nitrogen on the other, are mere phases of the great question of the fixation of nitrogen, and as the synthesis of one of these substances by the aid of atmospheric nitrogen would lead to the production of all, this limitation cannot exclude all considerations of these related substances.

The conditions essential to the fixation of nitrogen and the production of cyanides are indicated in the operation of the blast furnace, but only in the most general way. Neither observations nor experiment with the blast furnace have yet enabled any one to control it for the production of cyanides. The appearance of cyanides as a product of these furnaces, whenever observed, has occurred unexpectedly and has generally ceased as suddenly and mysteriously as it began. Bunsen's proposal, to erect a furnace similar to a blast furnace to be worked for cyanides only, has never been fully acted upon, and in the light of present experience it offers little promise of success. We have learned from the study of the blast furnace only that a high temperature, a reducing atmosphere, an alkaline flux and an excess of nitrogen are conditions favorable to the process.

The conditions most suitable in respect to temperature, flow of nitrogen, quality and density of carbon or carbonaceous fuel, proportion and nature of base, etc., are as yet undefined.

The more manageable furnace of Possoz and Boissiere (p. 13) although holding rather closely to the principle of the blast furnace, is free from its greatest defects in that it has no very deep column of coal to resist the flow of gases or crush the lower por-

tions into a compact mass by its weight. The air or nitrogen is admitted at many points also, and the cross section of the furnace is not small enough to prevent access of the gases to the centre of the column of coal. Its defects are, slowness of conversion of nitrogen into cyanogen, rapid destruction of the lining of the furnace, and contamination of the cyanides with silicates thereby formed.

The process of Margueritte and Sourdeval (p. 15) and that of Romily (p. 24) are each, for a different reason, free from the chief of these defects, yet they have been no more fortunate than their predecessors in finding a practicable, commercial process.

In order to reach a conclusion as to the present aspect of the whole question, it may be well to take up and consider in detail the various conditions upon which the absorption of free hydrogen by carbon depends, to see how far the theory of chemistry may lead us in anticipating the effect of each and to find, if possible, what combination of conditions gives, in the light of theory and past experience, most promise of success.

### 1. The Influence of Temperature.

Possoz and Boissiere (p. 13), to whom great deference is due as the authors of the most persistent as well as the most successful efforts ever made in this field, give unqualified testimony, as the result of long experience, to the necessity for very high temperatures. A white heat is said to be required and the fixation of nitrogen, other things being equal, is directly proportional to temperature. On the other hand, Armengaud and Ertel both claim that lower temperatures are quite adequate to effect the combination of nitrogen and carbon. Walter Weldon, also, one of the foremost authorities in the application of chemistry to manufactures of this or of any age, stated, in 1879, as the result of his own experiments, that the limit of temperature in this operation had been placed too high and that a red heat was sufficient. Siepermann, in 1887, testified to the same effect, basing his views on a series of experiments.

The question at issue relates only to the difference between a cherry red and a white heat, but this difference is of the utmost

importance in the practical operation of a plant, and may of itself be the point upon which the whole question will ultimately turn. It is possible, however, that, under conditions, either of the above views may be correct and the question must remain an open one until the process shall have been more fully studied.

## 2. The Influence of Oxygen.

It is generally admitted, as the result of all experiments upon the manufacture of cyanides, that oxygen and cyanogen cannot exist together at high temperatures. Theory leads to the same conclusion. Cyanogen is a combustible substance and the effect of oxygen upon cyanides is either, in the case of the alkaline cyanides, to convert them, first into cyanates and then into carbonates, or in the case of cyanides of the heavy metals, to decompose them with liberation of carbon monoxide and dioxide. All processes, therefore, using air as a source of nitrogen, provide for absorption of oxygen or its conversion into oxides of carbon. The mixed gases of the cyanogen furnace must be as a whole reducing, not oxidizing, in character.

## 3. The Influence of Water.

Here again we have P. and B. (p. 13) with their weight of practical experience insisting upon a condition which receives little support from others. It is evident, however, that the conditions of their furnace did not prevent the exclusion of moisture to such an extent as to decide the question absolutely, and the ill effects of water when admitted purposely and in greater quantity may be ascribed, in great part, to its cooling effects merely, when we remember the great expenditure of heat under which water is decomposed by carbon. Water in excess, also, decomposes cyanides, yielding ammonia. The experiments of Langlois are quite conclusive as to the principle that water in moderate quantity does not influence the production of cyanides, and Armengaud, Ertel and others (p. 15) speak positively as to its advantages. If the formation of ammonia is a preliminary stage in the synthesis of cyanogen, as Kuhlman suggests (p. 22), the presence of hydro-



gen, or, what is in effect the same, of vapor of water, is a necessary condition. Vapor of water is an oxidizing agent under certain conditions of temperature and for certain elements, but it is possible that cyanogen is not attacked by it at high temperatures in presence of hot carbon, carbonic oxide or hydrocarbons. The conclusions of several experimenters that water does not hinder the formation of cyanides is not, at any rate, definitely contradicted by theory.

#### **4. Time of Contact Between Nitrogen and Carbon and Degree of Subdivision of Carbon.**

If we assume that the base, which is found to be necessary in production of cyanogen from nitrogen of the air, combines instantly with the nascent cyanogen, the question of time is one simply of the speed of the preceding reaction between nitrogen and carbon. Chemical action between a solid and a gas, when the temperature necessary for the reaction has been attained, depends principally upon the surface exposed. The action may be assumed to be instantaneous like the action of oxygen upon hot and finely divided carbon and to be retarded only because the products of combustion cannot be removed from the sphere of action at the same rate at which the action takes place.

In a process like that of Possoz and Boissiere, and when each fragment of charcoal is bathed in a film of fused potash, action is limited by the rate at which the fused cyanide circulates in the pores of the charcoal and gives place to unchanged potash on the surface. New surfaces of carbon for attack, or of potash for absorption, are therefore exposed less frequently than is required, and complete saturation, that is, conversion into cyanide, is attained only after a long exposure and with much waste of gas and heat. The absorption of nitrogen is probably also retarded progressively as combustion proceeds, both because the pieces of carbon are reduced in size and therefore facilitate clogging of the flow of gas, and because the potash and fused cyanide are relatively more abundant as carbon decreases and lesser surface of carbon is exposed.

Both practice and theory, therefore, lead to the conclusion that,

other things being equal, the process will be hastened by any arrangement that tends to increase the surface of carbon exposed. The use of pulverized fuel would seem to be the ideal condition so far as carbon is concerned, and with an excess of ammonia, the only gaseous alkali, would probably, at a proper temperature, yield ammonium cyanide readily, as shown in Romily's experiment (p. 24) in which a smoky flame of hydrocarbon gas burning in air yields ammonium cyanide when the gas is charged with ammonia.

The effect of supplying the base also in the condition of powder would probably be to still further facilitate the action, as gaseous cyanogen would meet solid particles of highly heated base as soon as formed, and would combine with the metals of these bases to form cyanides. Alkalies would fuse and would probably tend to produce aggregations with particles of carbon, to that extent impeding access of air to them, but when we take into account the increased rapidity of chemical action under these conditions and the short time given to each group of particles in passing through the furnace, the gain by the process of pulverizing will probably be greater than the loss. Solid bases, like lime or baryta, are free from the latter objection, but also have less chemical energy.

### 5. Influence of Alkalies or Other Bases.

The influence of a base upon the union of carbon and nitrogen, both being in contact with the base and at a temperature sufficiently elevated for combination to occur, is probably due merely to the fact that the base serves to remove cyanogen from the sphere of action as fast as it is formed. The belief in a predisposing affinity, a non-correlated power, acting from a given centre to bring about a reaction in which the predisposing body has no share except to combine, *subsequently*, with the products of the reaction, is an ingenious fiction of the older chemistry, which finds little support at the present time. The influence of a foreign substance in impeding the union of two bodies by lessening the opportunities for contact of their respective atoms within a given time supplies a more tangible explanation. Every chemical reaction is limited

in violence after the first moment of action—is impeded and finally checked—by the products of the reaction, unless these are removed. Like any foreign substance these substances impair the freedom of access of the reacting atoms to one another and absorb heat which is necessary to the reaction. Whatever tends to remove these products quickly from the field of action tends to facilitate the reaction itself. When  $a$  and  $b$  unite to form  $ab$ , the presence of a third substance,  $c$ , capable of combining with the compound  $ab$  to form  $abc$ , but not with  $a$  or  $b$  separately, will facilitate the union of  $a$  and  $b$ , for the above reasons.

. This would seem to be the function of the alkali or other base in the synthesis of cyanogen. The conclusion is sustained apparently by the experiment of Langlois and the earlier chemists (pp. 10, 21–22), in which ammonia passed over hot charcoal yields ammonium cyanide. Trommsdorff first suggested that it was the presence of ammonia that favored here the formation of cyanogen by furnishing a means of fixing it as soon as formed.

The theory of the action of bases, of alkalies at least, is susceptible of another explanation. Many authorities (Bromeis, Bunsen and Playfair, Graeger, Rieken *et al.*, pp. 7, 10, 14, 22) believe that the union of carbon and nitrogen occurs only at or above the temperature at which potassium is reduced from its oxide by carbon. Metallic potassium or its vapor must be taken into account upon this hypothesis when the reaction in question is studied. This view would explain the lesser activity of soda in forming cyanides, as it is less readily reducible. Graeger (*Jsb. chem. Tech.*, 1858, 81) finds that in the old fusion process for prussiates the yield is lessened in proportion as potash is replaced by soda, even at temperatures approaching the fusing point of the cast iron pot. He believes that nitrogen from the organic matter in this case is volatilized and lost before metallic sodium is formed, owing to the high temperature required for reduction of sodium. Lime and baryta, from their infusibility, are also difficult to reduce, and should be less suitable for the process. Knowing the incompatibility of cyanogen and oxygen at high temperatures and the fact that cyanogen unites directly with the metals, it is quite possible that cyanogen can only combine when the metal itself is presented to it, and cannot

reduce the oxide, at least only by being itself destroyed. Bunsen and Playfair held (p. 18) that cyanogen in the upper part of the iron furnace acted as a reducing agent and was itself destroyed in reducing oxides of iron.

The theory of Berthelot (p. 16) is interesting in this connection. He holds that a direct compound of potassium and carbon ( $C_2K_2$ ) is formed and that this compound absorbs nitrogen, forming with it potassium cyanide. The theory is in perfect accord with the preceding one. Delbruch (p. 10) has also shown that cyanogen is formed when a mixture of nitrogen or ammonia with carbon dioxide is brought in contact with fused potassium.

It is possible also, that potassium or other metal, under these conditions, unites directly with nitrogen to form nitrides which then combine with carbon, yielding cyanides. The observation of Briegleb and Geuter, already referred to (p. 19), that magnesium nitride, when heated with carbonic oxide or carbonic acid evolves cyanogen, lends color to this view.

#### 6. The Nature of the Base to be Used.

As far as experiments have gone, potash seems to be the base best suited. Its great chemical energy and ready fusibility and reducibility in presence of carbon give it advantages over all other bases. Soda, besides being somewhat less powerful as a base, fuses at a higher temperature and therefore involves increase of wear and cost in apparatus. On the other hand it is cheaper, weight for weight, than potash, and, in addition, its lower molecular weight enables it to do more work for a given weight than potash in the proportion of 138.2 to 106.

The facility with which ammonium cyanide is formed when ammonia is passed over hot charcoal indicates that ammonia, like the fixed alkalies, combines very readily with cyanogen. It has the advantage of not acting as a flux upon the material of the furnace. The use of ammonia, itself produced from nitrogen of the air, to facilitate the synthesis of cyanogen at a lower temperature than that thought necessary for cyanogen alone, is suggested by Romily's experiment and may be a feature of future development in the fixation of nitrogen.

Of the infusible bases the alkaline earths, lime, baryta, strontia and magnesia only, seem to have sufficiently strong basic power to form cyanides with the air. The cyanides of other metals decompose quite readily when heated. The advantages of the alkaline earths are their infusibility, which prevents clogging of the mixture of coal and basic substance and so permits perfect access of nitrogen, and their cheapness. The corresponding cyanides are soluble and easily converted into alkaline cyanides. These qualities compensate to some extent for the deficient chemical energy of the alkaline earths. Margueritte and Sourdeval (p. 20) found that baryta absorbed nitrogen rapidly and that barium cyanide yielded ammonia on treatment with steam. Siepermann (p. 23) mixes baryta with alkalies to prevent fusion and clogging. Lime, the cheapest of these bases, seems to have been little used. Armengaud speaks of using it in his apparatus in 1843 (p. 20) and Fleck (p. 23) claimed the discovery that hot calcium hydrate could convert a mixture of nitrogen and carbonic oxide into ammonia and carbon dioxide.

#### **7. The Relation of Ammonia to Cyanogen and the Conditions which Determine the Formation of One or the Other.**

The production of ammonia by bringing together at a high temperature carbon, air or nitrogen, steam and a basic substance has long been known. The history of the subject although closely related in many respects to the question in hand has been omitted in this discussion for want of time. It is, however, difficult to separate two questions which deal, in a certain sense, with different phases of the same reaction. If any definite conclusion can be drawn from the results of industrial experiments it is that higher temperatures favor the production of cyanides and lower temperatures, of ammonia, with the addition also that vapor of water in excess is certainly unfavorable to the productions of cyanides but probably favorable to the production of ammonia. It is possible even that, for a temperature sufficiently high, supposing that it could be maintained against the cooling effect

involved in the decomposition of water by hot carbon, the proportion of water above or below a given limit might be the condition determining the production of ammonia in one case or cyanides in the other. It is difficult in the present state of our knowledge upon the subject to mention any conditions, other than variation in temperature and variation in quantity of water, which can account for the production at one time of ammonia and at another of cyanides in a furnace using in both cases precisely similar materials. The belief of Berzelius, Wöhler, Bromeis and others (pp. 7, 9), that formation of ammonia was the preliminary stage in the synthesis of cyanides and that water acted as an intermediary, accords with this view. An excess of water both by lowering the temperature and by impeding contact of nitrogen and carbon would retard the formation of cyanides and proportionally increase the ammonia.

The extraordinary permanence of ammonium cyanide, in comparison with other ammonium salts, at high temperatures (p. 22), (taken in connection with the fact that ammonia by itself is dissociated at high temperatures) may indicate that at very high temperatures ammonia can resist dissociation only in presence of a more refractory substance, hydrocyanic acid, with which it can combine. Ammonia in contact with coal, at a very high temperature, forms ammonium cyanide (p. 21, 22). This may be taken to mean that ammonia is more unstable in presence of hot carbon at that temperature than when merely heated alone, and that the portion first decomposed forms hydrocyanic acid which unites at once with a portion of ammonia not yet decomposed (because not yet in contact with hot carbon) and thus, in forming the stable compound ammonium cyanide, the ammonia is protected from dissociation or chemical decomposition. But if ammonia is *decomposed* at these temperatures it is unlikely that it can *form* under the same condition, while it is evident that cyanogen not only can but does form. We are led then to the hypothesis that, other conditions remaining unchanged, temperature is an important, if not the leading condition, which determines the production, respectively, of ammonia or cyanogen.

With respect to water as a determining cause, it may now be said that while an excess of water probably tends more and more

to oxidize or otherwise decompose cyanogen<sup>1</sup> as fast as it is formed at very high temperature its influence would be merely mechanical in retarding the formation of ammonia at a temperature somewhat lower. When the temperature is sufficiently high to enable carbon to decompose water one of the products of decomposition (CO) is without influence upon the formation of ammonia, while the other, hydrogen, is in the nascent state and therefore in the condition most favorable for union with nitrogen irrespective of the presence of carbon. If water were in a state of dissociation due to heat alone, oxygen coming from water could not, under those conditions, act upon ammonia, since it could unite neither with hydrogen or nitrogen. The case may be stated as follows :

*a.* Ammonia is not permanent at very high temperature, except in combination with cyanogen but is permanent at somewhat lower temperatures, still above a red heat. It is not decomposed by water at any temperature, but at certain temperatures its formation will be favored by the very conditions that make water an unstable compound, *i. e.*, high temperature and presence of carbon.

*b.* Cyanogen is permanent at very high temperatures with or without presence of ammonia. Cyanides are probably decomposed by water in excess at very high temperatures.

Finally, the presence of water in moderate quantity at certain elevated temperatures may favor the production of cyanides by permitting a certain formation of ammonia which is then converted into cyanides, the temperature being lower on the whole than that required for the formation of cyanogen without water. Here ammonia clearly acts as an intermediary, but the temperature, being above a certain limit, favors the production of cyanides rather than ammonia as the final product. At a slightly lower temperature—still, however, above the point at which water is decomposed by carbon—ammonia would form in preference to cyanides and in greater quantity ; with an excess of steam ammonia would

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<sup>1</sup> Karmrodt found that steam passed over hot potassium cyanide caused evolution of ammonia and the heated residue no longer contained cyanogen.

be the sole product. This may suggest the possibility of working a furnace intermittently with changes of temperature for the production in succession of cyanogen and ammonia or, what is the same in principle, the working of two furnaces in conjunction, one to produce ammonia and the other to convert this ammonia into cyanides.

### 8. The Influence of Other Gases Upon the Absorption of Nitrogen by Carbon.

The influence of carbon monoxide and carbon dioxide cannot be definitely stated. Bramwell expressed a preference for the latter in his cyanogen retorts, along with nitrogen, but it is hard to find any reason in theory for this preference, since the higher oxide of carbon is always reduced to the lower in presence of hot carbon and must be so changed in the cyanogen furnace. As it is therefore, an oxidizing agent, it should in theory, be more objectionable than carbon monoxide. It is more probable that foreign gases, provided they have no oxidizing character, merely impede the access of nitrogen to carbon and only act mechanically to retard the union of carbon and nitrogen.

It may perhaps be expected that the above theory should also explain why cyanogen is not formed in a coal fire by simple union of carbon and nitrogen. In the first place it has never been definitely settled that it does not. Many authorities (Binks, R. Wagner, Brunquill) have held with greater or less force to the belief that it does, or at least that it may so form under certain conditions. That it does not form readily or abundantly must, however, be conceded. Again the instability of cyanogen itself may be such, under the conditions of an ordinary fire, that it is decomposed as fast as formed, and its instant fixation by combination may be essential to its formation in appreciable quantities. The effect of fire gases, carbon dioxide or monoxide, sulphur dioxide, etc., upon free cyanogen has never been investigated, although several of the authorities already quoted have, from their own experience in the synthesis of cyanides, indicated a belief in



the influence of one or other of these gases upon the process (p. 15-16).

### 9. The Influence of Hydrocarbons in the Preparation of Cyanogen or Ammonia.

If hydrocarbon gases or vapors of heavy hydrocarbons were brought into a furnace containing the materials for production of cyanides or ammonia, namely, hot coal, nitrogen, water in greater or less quantity and an alkali or other basic substance, the result would be a partial decomposition or dissociation in which carbon, and hydrogen would be set free, and fixed gases having the composition of the lower paraffines or olefines would remain. Heavy hydrocarbons, oils like crude petroleum, might be used in part to supply the carbon necessary to the reaction; being in a condition of most minute subdivision as set free from combination, it would be most suitable for rapid combination. It is possible also that hydrogen liberated at the same time and in the nascent state would be better adapted to the synthesis of ammonia than at any other time, and further, this hydrogen would be obtained at less expenditure of heat than hydrogen from decomposition of water by carbon. The condition of a furnace fed with hydrocarbon vapors would resemble to a great extent the smoky gas flames of Levoir and Romily, (p. 23-24) in which ammonium cyanide was produced even without the intervention of a base other than ammonia.

### 10. The Influence of Pressure.

The data derived from experiment on the large scale give little information upon this point. Newton remarks (p. 11) that the production of cyanides is improved by a certain pressure and by friction between the solids and gases of the furnace, but this remark applies to very low pressures such as depend merely upon friction in retarding the gases as they are drawn or forced through the alkaliized charcoal by a pump. There is no evidence of systematic use of high pressures, exceeding one atmosphere for example, and the furnaces thus far designed for making

cyanides or ammonia are none of them adapted to the use of pressure. It is possible that the necessary reaction would be much assisted by pressure. There is every analogy indeed to favor this view. Combustion in compressed air or oxygen is more rapid than at normal pressure; and the union of nitrogen and carbon should be also accelerated. More of the unlike particles are brought in contact in a given time, and the opportunities for combination being multiplied combination should occur in the same proportion. Moreover the heat lost in expansion of gases is lessened and the temperature within the furnace should be more readily maintained.

If it were possible to maintain a pressure of several atmospheres within a furnace while the gaseous contents of the furnace were continually supplied and discharged, there is every reason to believe that the furnace would be more economical and more effective in the production of cyanides or ammonia.

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#### SUMMARY.

The present aspect of the question may be summarized as follows:

The manufacture of cyanides and ammonia from the nitrogen of the air, while quite possible on the small scale, is beset with difficulties in its economical and commercial application, which, up to this time, have been insurmountable. These difficulties are probably matters relating mainly to construction and to endurance of materials.

At the same time there is still much uncertainty in regard to the chemical and physical conditions most favorable to the fixation of nitrogen.

The following conclusions are the result of the foregoing inquiry:

1. The temperature necessary for formation of cyanogen may be lower than at first supposed, but certainly not below a high red heat. For ammonia a low red heat is sufficient.
2. The presence of free oxygen is deleterious in all cases.

3. Water in very small quantities is not prejudicial to production of cyanogen, and an excess is probably necessary in the synthesis of ammonia.

4. The long-continued contact of carbon and nitrogen is of less importance than thorough commingling of all reacting materials.

5. The presence of a strong base is essential, but under certain conditions ammonia, produced synthetically, may serve the purpose of a base and effect the synthesis of ammonium cyanide.

6. Alkaline bases are preferable, potash especially, and probably because of the intermediate action of metallic potassium, which is reduced at a lower temperature than sodium. Baryta is the best of the alkaline earths for the purpose.

7. Ammonia and cyanogen are probably formed under conditions differing in respect to temperature and moisture, but otherwise similar, as already indicated. (2.)

8. The presence of carbonic oxide and of reducing gases in general is probably favorable, while oxygen, carbonic acid and steam in excess (the latter only in the case of cyanogen) are probably injurious. Nothing is known as to the influence of sulphurous acid or hydrogen sulphide, but they are probably undesirable.

9. The presence of hydrocarbon vapors is favorable, and may, under certain conditions, permit the formation of both cyanogen and ammonia without the presence of a base.

10. There are no direct data for estimating the influence of pressure upon the reactions in question. The application of pressure is at least worthy of trial.

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#### DISCUSSION.

Dr. Waller said that the so-called "catalytic action" afforded no explanation of the effect of certain elements in the cyanogen forming process, and mentioned the apparent inducements offered for the production of a salt by the presence of a base, as for instance, the formation of calcium chromate by heating chrome iron ore with lime.

Dr. Alsberg called attention to the fact that addition of lime would in some cases contribute merely physical conditions which would aid in the reaction, such as porosity, infusibility, etc. Also that frequently in such instances of so-called catalytic action the temperature of formation and of dissociation of the new compound are so nearly the same that unless a base is present to unite with and retain it, as a salt not dissociated at that temperature, no reaction results. He expressed it as his opinion that not even a momentary formation of such compounds takes place under such temperature conditions unless in the presence of a base to retain them. The addition of iron in the cyanogen process has something to do with its success—as in the Castner sodium process.

Dr. Doremus referred to the production of oxygen from  $\text{KClO}_3$  and  $\text{MnO}_2$ , and to a paper published in the *Chemical News* intended to show the existence of a number of definite successive reactions between these substances. Experiments made with indifferent substances—*e. g.*, sand—substituted for  $\text{MnO}_2$ , gave dissimilar results.

Mr. Sabin: The escape of nitrogen as ammonia in the old prussiate process may be very great if the management is unskillful. A cyanide is first formed and then, at a higher temperature or on prolonged heating, ammonia is produced. I believe that in a properly constructed and continuously acting furnace all of the nitrogen of leather scrap could be converted into ammonia in presence of caustic soda and moisture, although the process might not be economical. I doubt whether any cyanide manufacturers in this country, with one exception, are making a paying business of it, as such large quantities of cyanides and ferrocyanides are imported. The exception, a firm in Newark, are using an improved pear-shaped retort heated only at the central wide portion.

Dr. Alsberg: We are on the eve of a complete revolution in prussiate processes; cyanides and ferrocyanides are manufactured in Germany from gas purifier waste in such quantities as to have reduced the price 25 per cent. The process of making cyanides from sulphocyanides is not easy because of difficulty of eliminating sulphur. The only practical process at present is by heating sulphocyanides and finely divided iron under pressure

at 120–140°C., whereby ferrocyanide and ferrous sulphide are formed. It is also stated that if a sulphocyanide and ferrous sulphate are mixed and exposed to air, that sulphur is gradually taken up in presence of free alkali, but it seems somewhat doubtful. The old method of making cyanides will have to be abandoned for cheaper methods. Sodium ferrocyanide is now made in large quantities to replace potassium ferrocyanide using gas house wastes and commercial soda ash. More of sodium bichromate is used in dyeing and calico printing than of potassium bichromate, but certain colors, it is claimed, will not permit of the substitution.

Dr. Doremus said the Wilkinson process for manufacturing wood gas produced little cyanogen and no ammonia; in fact he had never heard of either as impurities requiring any attention.

Prof. Breneman: The formation of ammonia by an ordinary coal fire may not be impossible. In the gas retort the amount of ammonia and cyanides produced is very large, possibly larger than that due to the nitrogen in the coal alone, although the access of atmospheric nitrogen, through leakage and at time of changing, cannot be very free.

\* In regard to the question of action by presence or predisposing affinity, the case, in its strictest sense, is inconceivable. It involves action *for a purpose* by inanimate things. Also, the supposition that action of a certain kind cannot take place, even momentarily, under conditions in which decomposition also occurs, is a necessity only in theory. It presupposes that every newly formed molecule is instantly solicited by all of the conditions, chemical and physical, that affect the mass, whereas in a reacting mass of *solids* (less so in the case of liquids or gases, although still existing) there are difficulties in the way of instant diffusion of all conditions. Heat may be locally increased or decreased momentarily by chemical action, and *vice versa*, and these changes may favor the local formation of products which are instantly fixed by active substances present in excess, as has been already explained (p. 38).—A. A. B.

## NOTES ON THE ANALYSIS OF ZINC ORES.

BY E. WALLER, PH. D.

The time at my disposal for these experiments has been limited, and has constantly been broken in upon, so that what is presented will, I trust, be regarded with indulgence; more as a sketchy account of experiments on this subject than as a thorough investigation.

The object was to attempt to find or to invent a convenient and fairly rapid method of general applicability for the determination of zinc in its ores. Experiments were first made with Schneider's method. A Franklinite ore containing copper, and said to contain about 30 per cent. of zinc, was used. Schneider's method (*Ztschr. anal. Chem.*, **23**, 562), may be thus sketched. Treat 1 gm. of ore with 10 c.c. conc. sulphuric acid, together with 1 or 2 c.c. conc. nitric, heat until strong fumes of  $\text{SO}_3$  appear; dilute carefully with 70 c.c. of water, pass sulphuretted hydrogen for 15 minutes through the hot solution, heat to boiling, filter and wash until a volume of about 200 c.c. is obtained, add ammonia to the solution (heated) until a slight cloud persists, bring this into clear solution by addition of a few drops of sulphuric acid, dilute to 500 to 600 c.c., and pass  $\text{H}_2\text{S}$  for an hour. Under these conditions Schneider states that zinc only is precipitated.

Some difficulties manifested themselves in applying this method to the ore selected. However finely pulverized, the decomposition of the Franklinite appeared incomplete. Diluting with 70 c.c. of water seemed to be insufficient, a small amount of the copper remaining in solution and appearing with the zinc; when the stage of separation of the zinc was reached, passing sulphuretted hydrogen for one hour, was found to be too short a time for complete separation. The precipitate also was not in a condition that permitted of its being readily filtered and washed. It also

appeared colored, and some phenomena gave rise to a suspicion that it contained manganese as well as copper, but through inadvertence, tests were not made for Mn. The percentage of zinc obtained by this method was from 25 to 25.4. If the ore was really 30 per cent., five per cent. had been lost.

With the expectation of decomposing the ore more completely at the start, a portion of the ore was first heated with hydrochloric acid (about 10 c.c.) and then sulphuric and nitric acid added, and Schneider's method followed through as before. The decomposition of the ore was apparently complete both from the appearance of the insoluble residue, and the percentage of zinc obtained (30.03 and 29.92), but the plan had its objections both as to the time and the attention it required. Hydrochloric acid caused the separation of gelatinous silica, which retarded the action of the acids, and in driving out the HCl afterward by heating with  $\text{H}_2\text{SO}_4$ , at a certain stage the solution bumped violently, and required constant attention.

The addition of hydrochloric acid at the same time with the other acids, carrying the rest of the process through as before, seemed to have all the disadvantages of the preceding experiment, without any gain in the completeness of decomposition of the ore. The percentage of zinc found was as before, about 25.

With a view to effecting a more complete separation of the copper, the solution after the first dilution (with 70 c.c. of water), was cooled before passing sulphureted hydrogen. The last traces of copper were, however, not thus removed. The proportion of copper present in the ore was small, however (probably 0.2 per cent.), or at any rate less than 0.5.

A solution containing most of the zinc in the ore, and the other constituents excepting copper and silica, was then made, and experiments made as to the separation of the zinc without a preliminary removal of the iron, manganese, etc.

Ribau's method (*Bull. Soc. Chim.*, 50, 518) was followed on one portion, as prescribed by him. Sodium carbonate was added until a faint permanent turbidity was produced, a few drops of hydrochloric acid were then added to clear the solution, then an excess

of sodium hyposulphite, and the solution was diluted until it contained less than 0.1 gm. of zinc per 100 c.c. Sulphuretted hydrogen was then passed through, *in the cold*. The precipitate, instead of being pure, white zinc sulphate as described by Ribau, was dark gray, being evidently contaminated with iron. Variations in the proportion of hyposulphite, or in the degree of dilution, had no effect in preventing completely this contamination of the precipitate, so far as could be seen. Zimmerman's suggestion (*Chem. News*, 40, 273), to neutralize the solution, add an excess of ammonium sulphocyanate, and precipitate by sulphuretted hydrogen, warming the solution, gave the most satisfactory results as to rapidity of separation of the precipitate, its purity and its granular condition, allowing of ready filtering and washing. With some other zinc ores, however, it did not seem to work so well, but experiments remain yet to be made as to the cause of this difference of action, completeness of precipitation, etc.

The partial success with this last suggested a trial of the method recommended by Moore for the separation of zinc and nickel by means of KCy and ammonium sulphide (*Chem. News*, 49, 151). The precipitate proved to be very slimy, and contained prussian blue, and for these and other reasons experiments in this direction were abandoned.

Bragard's method (*Ztschr. anal. Chem.*, 27, 209) of precipitation with sulphuretted hydrogen in a solution containing formic acid was tried, but thus far with poor success. The proper ratio between the amounts of formic acid, of the metals present, etc., was probably not obtained.

On that method it will be necessary to make more experiments. The separation of the precipitate was very slow and unsatisfactory.

Incidentally I have been led to investigate the properties of zinc ammonium phosphate as a means for determining zinc.\* A few notes on the results may be of interest :

Solutions of pure metallic zinc in hydrochloric and sulphuric acid were used. A solution of microcosmic salt was used as the

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Stone, *Jour. Am. Chem. Soc.*, 4, 26. Tamm, *Ztschr. anal. Chem.*, 13, 320. Bragard, *ib.*, 27, 212. Lose Kam and Meyer, *ib.*, 26, 78.



reagent. A sufficient excess of the reagent was added, then ammonia until it was in excess, and then the solution (usually about 200 c.c.), was heated for an hour or more, until all odor of ammonia was gone, and the precipitate had assumed a crystalline character. The bumping of the solution on attempting to boil was so troublesome, that the plan of immersing the beaker in boiling water was adopted. The persistent adherence of portions of the precipitate to the sides of the beaker was another source of annoyance. This difficulty was avoided by washing thoroughly by decantation, and then dissolving in as little nitric acid as possible, running the solution through the filter paper into a weighed platinum dish, evaporating and then gradually heating up to the temperature of ignition. A too hasty application of the heat, or incineration of the precipitate in the filter paper, invariably caused a loss. After being once ignited to  $\text{Zn}_2\text{P}_2\text{O}_7$ , further ignition had no appreciable effect, nor was there any loss when pieces of filter paper were laid over the precipitate in the crucible and the whole heated until the paper was destroyed. The precipitate always sintered together under the influence of the temperature of ignition, and sometimes, without apparently having been heated any longer or to any higher degree, it fused to a vitreous mass.

0.511 grm. of the precipitate after drying at  $110^\circ$  to constant weight, weighed 0.4365 grm. after ignition. Assuming the dried precipitate to be  $\text{ZnNH}_4\text{PO}_4$  0.511 grm. should yield 0.43636 grm. of  $\text{Zn}_2\text{P}_2\text{O}_7$ .

The precipitate is quite soluble in ammonia, the solubility increasing rapidly with an increase of temperature.

Ammonium chloride and oxalate acted in the same way. From the ammonium chloride solutions, where they had been used hot, considerable quantities of the precipitate separated on cooling, but it was found that when 15 to 18 grms. or more of  $\text{NH}_4\text{Cl}$  were present in 200 c.c. of liquid, the results were too low though the solutions were kept cold, but with smaller proportions of  $\text{NH}_4\text{Cl}$  (5 to 8 grms.), the results were fairly good, with cold solutions.

Much larger quantities of microcosmic salt, of ammonium ni-

trate or of ammonium sulphate, had much less of a solvent effect. In the cold they dissolved apparently nothing appreciable. At some future day I hope to be able to report more complete results and conclusions on these subjects.

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## ABSTRACTS: ANALYTICAL CHEMISTRY.

### Determination of Tungsten in Tungsten Alloys. DR. JOS. PREUSSER.

Place .5–1 grm. of the finely pulverized alloy in a porcelain dish, and roast the alloy until it has assumed a pure yellow color, showing that the tungsten has been oxidized to tungstic acid. Rinse the mass into a porcelain evaporating dish, add nitro-hydrochloric acid and evaporate; continue the evaporation several times after addition of hydrochloric acid and finally dry at 120° C. Digest with dilute HCl for several hours and filter. Ignite the residuum (tungstic acid and silica) in a platinum crucible; mix intimately with 3–4 times its weight of sodium carbonate, and fuse for  $\frac{1}{2}$  hour. Cool, dissolve in water, and filter. Treat any residuum again with sodium carbonate as before. The combined alkaline filtrates containing the tungstic and silicic acids are super-saturated with HCl and evaporated. The residue should be several times evaporated to dryness after additions of HCl. Transfer the residue to an Erlenmeyer flask, removing any adherent matter from the porcelain dish by means of ammonium hydrate. Add excess of ammonia and heat gently, and finally filter, collecting the filtrate in a weighed porcelain dish. Evaporate to dryness and ignite to constant weight. The resulting product is tungstic acid. Much time is saved by the above method. (*Ztschr. anal. Chem.*, 28, 173.)

J. F. G.

### Determination of Phosphoric Acid in Sweet Wines. W. FRESSENIUS.

In determining  $P_2O_5$  direct in the ash of wines very rich in saccharine matter, considerable  $P_2O_5$  may be lost. It is advisable to remove the alcohol by evaporation, and then ferment the

saccharine matter by adding a little yeast. The  $P_2O_5$  can then be determined as usual. (*Ztschr. anal. Chem.*, **28**, p. 67.)

J. F. G.

**Arsenic in Bone Phosphate Fodder.** II. FRESSENIUS.

Arsenic may be introduced through impure acids. A suitable method to determine the arsenic is by distillation. Place 10 gm. of the substance in a retort, add 100 c.c. of strong hydrochloric acid (1.19 Sp. Gr.); when the phosphate has nearly dissolved add 5 c.c. of a saturated solution of ferric chloride, and distill until only a small residue remains. Precipitate the arsenic in the filtrate by  $H_2S$  and weigh as  $As_2S_3$ . Of 25 samples examined, all contained arsenic in quantities ranging from 0.028 per cent. to 0.17 per cent. (*Ztschr. anal. Chem.*, **28**, p. 64.)

J. F. G.

**Modification of Kjeldahl's Method.** DR. J. W. GUNNING.

The author recommends the use of acid potassium sulphate prepared by adding two parts of ordinary concentrated sulphuric acid to one part of potassium sulphate. This mass is semi-solid, but melts readily on warming. The special advantages claimed are that the acid is kept in a concentrated condition during the breaking down of the organic matter and therefore facilitates the decomposition. (*Ztschr. anal. Chem.*, **28**, 188.)

J. F. G.

**Butter Analysis.** L. F. WILSON.

In summarizing the results of the testing of 843 samples of butter fat the author arrived at the following conclusions:

a. Colostrum fat is very poor in volatile acids. In two cases the volatile fatty acids by the Reichert method required but 9.27 c.c. and 10.00 c.c. of  $\frac{1}{10}$  alkali.

b. The volatile acids in the fat increase rapidly after calving, reaching the normal again in 5-7 days.

c. The alkali required in individual cases varied from 20.5 max. to 11.45 min.

Out of 797 cases, 44 samples required less than 12.5 c.c., varying in 32 samples from 12.48 to 12.00 c.c., and for the remaining 12 from 11.93 to 11.45 c.c. (*Ztschr. anal. Chem.*, **28**, 175-183.)

J. F. G.

**Free Fatty Acids in Oils.** HUGO NOERDLINGER.

The free fatty acids in various "salad" oils varies from 0.47 to 5.75%. The average quantity for the different varieties does not exceed 1-2%:

"Salad" Rapeseed oil.....	1.19%
" Poppy oil .....	1.92%
" Earthnut oil.....	1.94%
" Sesamé oil .....	1.97%
" Olive oil .....	1.69%
<hr/>	
General average.....	1.74%

Good oils for salad purposes ought not to exceed the above averages.

To determine the free fatty acids dissolve the oil in a mixture of ether-alcohol containing phenolphthalein and titrate with  $\frac{N}{10}$  alkali. (*Ztschr. anal. Chem.*, 28, 182.) J. F. G.

**Analysis of Commercial Peptones.** J. KÖNIG AND W. KISCH.

The data for valuation are the determination of the per cent. of water, the different mineral constituents, soluble and insoluble albumen, per cent. of fat, and differentiation of the albuminoid constituents. The authors used the following methods: 5-10 grms. of the peptone are dissolved in water, filtered, the residue is collected on a filter and dried and the N is determined in the residue and filter by the Kjeldahl method. Per cent.  $N \times 6.25$  = insoluble albumen. The filtrate from the above acidulated with acetic acid and boiled. Any precipitate is collected and its N determined as above. Per cent.  $N \times 6.25$  = soluble albumen. For the fat, 10 to 20 grms. of the peptone preparation are mixed with a sufficient quantity of sand, dried and exhausted with ether. To differentiate between the albuminoid bodies the authors recommend precipitation by  $(NH_4)_2SO_4$  solution instead of ferric acetate.

*The filtrates from the soluble and insoluble albumen*—(take originally 5 grms. for solid, 10 grms. for syrupy and 20 grms. for liquid

peptone preparation)—dilute to 500 c.c. (A) and take, according to quantity of solids, 50–100 c.c., concentrate to 10 c.c. and precipitate the same with 100 c.c. of saturated solution of ammonium sulphate in the cold. After settling, collect the precipitate on a weighed dry filter, wash with saturated solution of ammonium sulphate, dry and weigh. Dissolve the contents of the filter in water, dilute to 500 c.c.; determine the  $\text{SO}_3$  in 100 c.c., after acidulating with  $\text{HCl}$ , by  $\text{BaCl}_2$ , and calculate to ammonium sulphate,  $(\text{NH}_4)_2\text{SO}_4$ . Deduct the result from the increased weight of the filter—the difference being the per cent. of albuminous constituents.

Of solution (A) above, take 50 c.c. to 100 c.c., acidulate strongly with sulphuric acid and then precipitate by additions of solution of sodium phospho-tungstate (3 parts of the acid sodium phospho-tungstate solution to 1 part of dilute sulphuric acid) until no more precipitate forms, filter, wash with dilute sulphuric acid (1:3), and while still moist, transfer the washed filter and contents to a flask, and determine the nitrogen by the Kjeldahl method.  $\text{N} \times 6.25 = \text{albumens} + \text{peptone}$ . Deducting that found by the  $(\text{NH}_4)_2\text{SO}_4$  precipitation = peptone. The precipitation by the ferric acetate, etc., method may yield a higher percentage of peptones, but the  $(\text{NH}_4)_2\text{SO}_4$  method is considered to yield the more accurate results. (*Ztschr. anal. Chem.*, 28, p. 191–201.)

J. F. G.

REGULAR MEETING, April 5th, 1889.

Vice-President A. A. Breneman in the chair.

Morris Loeb, Ph. D., of Newport, R. I., was unanimously elected  
a member of the Society.

Mr. Wm. R. Potter was nominated for membership.

Dr. Kent made some remarks upon the detection of tin salts in  
molasses.

Some general discussion followed.

The meeting then adjourned.

DURAND WOODMAN.

Recording Secretary.

Dr.	From January 1st to December 31st, 1888.	Cr.

\* This statement should have appeared in January number but has been delayed by the illness of the Treasurer. Ed.

## POLARISTROBOMETRIC-CHEMICAL ANALYSIS.

BY H. LANDOLT.\*

†Translated by J. F. GEISLER.

## INTRODUCTORY.

In determining the rotatory power of optically active substances in solution the following factors are of practical bearing :

a. The observed angular rotation of a ray of light (usually D) by a solution at a definite temperature (generally 20°).

l. The length of the tubes used (in decimeters).

d. The sp. gr. of the solution (generally determined at 20°, calculated upon water at 4°).

p. The %, *i.e.* the weight of active substance in 100 parts by weight of the solution.

q. The % of optically inactive substance.

c = pd the concentration, *i.e.* the number of grammes of active substance in 100 c. c. of the solution.

From these the sp. rotatory power is found by

$$([\alpha] = \frac{100a}{lc} = \frac{100a}{lpd}) \quad (1)$$

which gives the angular rotation which a column of the solution 1 dm. in length would cause, if each c. c. contained 1g of the optically active substance.

The sp. rot. power is affected not only by the wave length of the ray of light and the temperature, but usually also by the nature of the solvent as well as the percentage (p) and the concentration (c).

The increase or decrease of the specific rotation of nearly all optically active substances, which is shown by the varying composition of the solutions and attributable to the action of the solvent upon the active molecules, may be represented by :

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\* *Ztschr. anal. Chem.*, 28, p. 208-218, from *Ber. d. chem. Ges.* 21, p. 191.

†Owing to the importance and general usefulness of this branch of analytical chemistry, this paper, which tends to systematize the methods and introduce correct formulas for calculating polaristobometric analyses is given almost complete. J. F. G.



1. The percentage-content of inactive solvent

$$[\alpha] = A + Bq + Cq^2 \quad (2).$$

2. The percentage content of active substance

$$[\alpha] = a + bp + cp^2 \quad (3).$$

3. The concentration

$$[\alpha] = \mathfrak{A} + \mathfrak{B}c + \mathfrak{C}c^2 \quad (4).$$

If the constants of the equations (2) and (3), determined by the examination of a number of solutions, are to be transposed, we have

$$\begin{array}{l|l} a = A + 100B + 10000C & A = a + 100b + 10000c \\ b = -B - 200C & B = -b - 200c \\ c = C & C = c \end{array} \quad (5).$$

Formula (3) may be used for calculating the concentration and (4) for percentage-content when the sp. gr. of the solution is known, and by using  $p = \frac{c}{d}$  or  $c = pd$ .

If for an active substance whose molecular weight is  $M$ , the constants in the equation (3) have been determined by trial, and these latter are to be calculated so as to represent one derivative affected by the molecular weight  $M_1$ , and whose formula shall be  $[\alpha]_1 = a_1 + bp + c_1 p^2$ , then all the quantities of equation (3) must be multiplied by the factor  $\frac{M}{M_1}$  whence for the new constants

$$a_1 = a \frac{M}{M_1} \quad b_1 = b \left( \frac{M}{M_1} \right)^2 \quad c_1 = c \left( \frac{M}{M_1} \right)^3 \quad (6).$$

For changing Ventzke's saccharimeter degrees into angular degrees for the ray (D) the ratio is usually taken as

$$1^\circ \text{ Ventzke} = 0.3455 \text{ degrees (sodium light)}.$$

This ratio varies, however, for different substances, so that when accuracy is required, the factor should be determined by comparisons with the respective instruments. Thus

1° Ventzke (Gas light) =

Cane sugar.....	0.3465 ± 0.0005	degrees (Na flame).
Milk sugar.....	0.3452 ± 0.0002	“ “
Grape sugar.....	0.3448 ± 0.0008	“ “
Invert sugar.....	0.3432 ± 0.0007	“ “
Cholesterin .....	0.3416 ± 0.0012	“ “
Turpentine .....	0.3494 ± 0.0009	“ “

The values are, moreover, affected somewhat by the degree of concentration.

The values for the concentration will be affected somewhat by the value of the unit volume—*i.e.* the true c. c., or Mohr's c. c. In most of the scientific determinations of the specific rotatory power of optically active substances the true c. c. was used, *i.e.* the 100 c. c. mark on the flasks indicates the volume of 99.72g of water at 20°; the solutions were weighed out at 20°, and the specific gravities were determined at the same temperature based upon water at 4°. For saccharimetric work 100 c. c. flasks have come into use, which were prepared according to the directions of Mohr, accordingly the 100 c. c. mark indicates the volume of 100g of water at 17.5°. The latter volume is used in the preparation of the normal sugar (26.048g) solution, which on the Ventzke scale causes a deviation of 100°. Hence Mohr's c. c. (17.5°) ÷ 0.9977 will give the value for true c. c. at 20°. The sp. rot. powers determined with Mohr's concentration  $\left( \text{pd } \frac{17.5}{17.5} \right)$  would have to be multiplied by 0.9977 if the true c. c. is to be used as the unit volume.

Of the many compositions of which a solution may consist, the following shall be considered.

#### I.

*Solutions, which consist of but one active substance and an inactive solvent.*

The conditions here resolve themselves into two, according to

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\* At least for the instruments manufactured by Schmidt & Haensch in Berlin.

the greater or less degree to which the sp. rot. power is affected by the concentration.

A. If the determinations show that the sp. rot. power of the substance is permanent, *i. e.* proportional to the concentration, then the quantity (*c* or *p*) in an unknown solution is found by the equation

$$c = \frac{100a}{[\alpha]} \quad P = \frac{100a}{[\alpha]d} \quad (7).$$

The same formula may be used for substances in which the variations due to concentration are but slight, by substituting an average result for  $[\alpha]$ . The method may accordingly be used for the following substances:

1. Cane Sugar.—The well known method for determining cane sugar by means of the polariscope, or special saccharimeters, is based on the supposition that the ratio between rotation and concentration is uniform. The investigations of Schmitz and Tollens show, however, that the value of  $[\alpha]$  decreases as the concentration increases. Up to a concentration of  $C=30$  the variation may be shown by the formulas

$$[\alpha]_D^{20} = 66.67 - 0.0095 \left( \text{True c. c. d} \frac{20}{4} \right)$$

$$[\alpha]_D^{20} = 66.82 - 0.0096 \text{ c. c. d} \left( \frac{17.5}{17.5} \right)$$

Whence for

c. =	5	10	15	20	25	30
True c. c. $[\alpha]$	= 66.62	66.58	66.53	66.48	66.43	66.38
Mohr's c. c. $[\alpha]$	= 66.78	66.73	66.68	66.63	66.58	66.54

If an average factor is taken as

$$[\alpha]_D^{20} = 66.5 \text{ for true c. c., } [\alpha]_D^{20} = 66.65 \text{ for M. c. c.}$$

then the concentration may be found from the observed angular rotation by the formulas

$$c = 1.5038 \frac{a}{1} \text{ for t. c. c., } c = 1.5004 \frac{a}{1} \text{ for M. c. c.}$$

giving for the extreme percentage-content of 5 and 30g variations of respectively +0.01 and -0.05 from the true result.

If the variations are to be taken into account then the formula of Schmitz\*

$$c = 0.75063 a + 0.0000766 a^2 \text{ (true c. c.)}$$

may be used, in which  $a$  is the angular rotation observed in a 2 dm. column.

2. Milk Sugar.—Schmöger† found the specific rotatory power of solutions of milk sugar uniform up to a percentage-content of 36 ( $c = 41.5$ ) and gives for the hydrate  $C_{12}H_{22}O_{11} + H_2O$  the value

$$[\alpha]_D^{20} = 52.53^\circ \left( \text{t. c. c. d } \frac{20}{4} \right).$$

The rotation decreases as the temperature rises, and at about  $20^\circ$  the above value is increased or diminished 0.075 for each  $1^\circ$  temp.

The birotation which crystallized milk sugar shows shortly after solution can be changed to the constant by warming the solution. But if sugar dried at  $100^\circ$  is dissolved in cold water, the solution shows at first a lower rotation than the normal, which latter it attains after several hours on standing at ordinary temperatures or immediately after heating. Schmöger,‡ Erdmann.§

3. Maltose.— $C_{12}H_{22}O_{11} + H_2O$ . Dextro-rotatory. Meissl§ gives for the dependence of the sp. rot. power upon the  $\%$ -content of the water solutions and the temperature of the same the formula

$$[\alpha]_D^t = 140.375 - 0.01837 p - 0.095 t \left( \text{t. c. c. d } \frac{17.5}{4} \right)$$

which is true for variations of  $p = 5$  to 35 and  $t = 15$  to  $35^\circ$ .

Owing to the relatively small variation, by inserting an average factor

$$[\alpha]_D^{17.5} = 138.3 \text{ or } [\alpha]_D^{20} = 138.1$$

in formula (7) the error, even when  $p = 30$ , would be within hundredths  $\%$ .

\*Ztschr. d. V. f. d. Rübenzucker-Ind. d. D. R. 1879, 950.

†Ber. d. chem. Ges., 1880, 885.

‡Berr. d. chem. Ges., 1880, 1915, 2130.

| " " " " 1880, 2180.

§ Jour. f. Prakt. Chem. (II.), 25, 114.

4. Raffinose (Melitose).— $C_{18}H_{32}O_{16} + 5H_2O$ .

Dextro-rotatory.—The specific rotary power for water solutions were found by:

a. Scheibler, by means of a quartz-wedge-saccharimeter

$$[\alpha]_D^{17.5} = 103.9 \text{ to } 104.0 \text{ for } c = 5 \text{ to } 16.$$

b. Tollens, by means of a half shadow instrument and Na. light,

$$[\alpha]_D^{20} = 104.44 \text{ to } 104.0 \text{ for } c = 10.$$

c. Rieschbiet and Tollens,\*

$$[\alpha]_D^{20} = 102.41 - 104.9 \text{ for } c = 10.$$

d. von Lippmann  $[\alpha]_D = 104.96$  for  $p = 2.67$ .

e. Finally Tollens† calculates from the data of Losseau  $[\alpha]_D = 105.7$ , and of von Ritthausen  $[\alpha]_D = 104.0$ .

From which it appears that the sp. rotation is affected but little by the concentration, and that an average factor

$$[\alpha]_D^{20} = 104.5 \text{ may be used.}$$

In alcohol of 75% raffinose shows, according to Scheibler, the same rotatory power as in water.

Dextrose.—For the variations in sp. rot. power of dextrose solutions due to the % content of the solutions, Tollens supplied the formula

$$[\alpha] \frac{20}{D} = 52.50 + 0.0188.p + 0.00052.p^2 \left( \text{t. c. c. d } \frac{20}{4} \right)$$

$$\text{whence for } \begin{matrix} p = 5 & \text{etc.} & p = 30 \\ [\alpha] = 52.61 & & [\alpha] = 53.53 \end{matrix}$$

For solutions containing not over 20 g. in 100 c. c., the factor  $[\alpha] \frac{20}{D} = 53.0$  is satisfactory.

For greater concentrations more accurate results are obtained by the author's new formula,  $p = 0.948.a - 0.0032.a^2$ , in which  $a$  is the angular rotation observed in a 2 dm. column.

\* Ann. Chem. (Liebig) **232**, 169. Z. V. J. R. I., 1886, 214.

† Ann. Chem. (Liebig) **232**, 170.

The birotation of a fresh solution of dextrose is destroyed by heating, or by letting the solution stand for twenty-four hours.

6. Lævulose.—The lævo-rotation of the aqueous solutions increases with the degree of concentration and diminishes as the temperature rises. The only reliable data are those of Herzfeld\* and Winter† who used lævulose derived from inulin.

From these data it follows that the dependence of the sp. rotation at 20° temp. upon the %-content is expressed by

$$[\alpha] \frac{20}{D} = 69.53 - 0.0935.p \left( \text{t. c. c. d } \frac{20}{4} \right)$$

$$\text{whence for } p = 5 \quad - \quad - \quad - \quad 30$$

$$[\alpha] \frac{20}{D} = -70.00 \quad - \quad - \quad - \quad -72.34$$

According to Herzfeld‡, between the temp. of 20°—40° for each increase of 1° temp., the value of  $[\alpha] \frac{20}{D}$  is lowered 0.5° for %-content of 10 to 40.

According to Winter,§ lævulose dissolved in absolute alcohol, possesses a much lower sp. rot. power, namely,

$$[\alpha] \frac{20}{D} = -47.0 \text{ for } p = 7.78.$$

7. Invert Sugar.—The sp. rot. power of invert sugar obtained from cane sugar by the action of dilute acids, shows considerable variations, subject to the conditions of

(a.) The concentration.—Gubbe\*\* found that for aqueous solutions of invert sugar, prepared by heating cane sugar solutions (containing 1 part of oxalic acid for every 100 parts invert sugar) for several hours at 60°, the sp. rot. p. at the temp. of 20° depended upon the %-content of water, as follows:

$$[\alpha] \frac{20}{D} = -23.305 + 0.01648.q + 0.000221.q^2 \left( \text{t. c. c. d } \frac{20}{4} \right)$$

\* Z. V. f. R. Z. I., 1884, p. 445, and 1886, p. 114.

† Loc. cit., 1887, p. 797.

‡ Z. V. R. Z. I., 1884, p. 444.

§ Z. V. R. Z. I., 1887, p. 807.

\*\* Ber. d. chem. Ges., 1885, p. 2207.

Z. V. R. Z. I. 1884, p. 1345.

which for  $p$ . gives the formula

$$[\alpha] \frac{20}{D} = 19.447 - 0.06068, p + 0.000221. p^2.$$

This formula holds good for %-content up to  $p = 68$ .

For weaker solutions Gubbe gives for the concentration  $c$  the formula

$$[\alpha] \frac{20}{D} = -19.657 - 0.0361.c \left( t. c. c. d \frac{20}{4} \right)$$

which is true for  $c$  up to 35.

(b.) According to Tuchschnid the sp. rot. power diminishes 0.32 for each rise of  $1^\circ$  temp. between the temp. of  $5^\circ$  to  $35^\circ$ , when  $c = 17.21$ .

Gubbe gives the more accurate formulas :

$$t = C^\circ \text{ to } 30^\circ$$

$$[\alpha] \frac{t}{D} = [\alpha] \frac{20}{D} + 0.3041 (t - 20) + 0.00165 (t - 20)^2$$

$$t = 20 \text{ to } 100^\circ$$

$$[\alpha] \frac{t}{D} = [\alpha] \frac{20}{D} + 0.3246 (t - 20) - 0.00021 (-20)^2$$

(c.) The kind and quantity of acid used for the immersion, as well as the quantity of acid remaining in the solution. Gubbe found that oxalic acid did not affect the rotatory power, but hydrochloric and sulphuric acid increased it. The increased rotation in 9 per cent. solutions of invert sugar amounted to 0.362 per 1 g. hydrochloric acid, and 0.170 per 1 g. of sulphuric acid present.

For increased concentrations these variations are much diminished.

(d.) The time and degree of heat used during the inversion.

In Clerget's method the cane sugar solutions, to which are added 5% by sol. of concentrated hydrochloric acid (sp. gr. 1.88=38%), are heated for fifteen minutes at  $67-70^\circ$  and then rapidly cooled, Creydt\*. If heated longer or at a higher temperature, the rotation may be diminished on account of decomposition.

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\* Z. V. R. Z. I., 1887, p. 158.

(e.) The sp. rot. power of invert sugar is changed when acid-free solutions of invert sugar are evaporated in a vacuum to a syrupy consistency, probably owing to the formation of hydrated products (dextro-rotatory lævulosan?). On resolution dextro-rotation may be obtained, or at least a lævo rotation less than the normal. The latter may be reobtained by adding hydrochloric acid and setting the solution aside for several hours, or by heating for a short time at 67-70°.

(g.) Further, the rot. power of invert sugar solutions is affected by the presence of other substances such as alcohol, acetate of lead, or lime.

8. Galaktose (Lactose). Dextro-rotatory.—Meissl found that the specific rotatory power of aqueous solutions of lactose as affected by %-content and temperature, is expressed by

$$[\alpha] \frac{t}{D} = 83.883 + 0.0785 p - 0.209 t \left( t. c. c. d \frac{17.5}{4} \right)$$

which equation is good for

$$p = 5 \text{ to } 35, \text{ and } t = 10^\circ \text{ to } 30^\circ.$$

Rindell gives

$$[\alpha] \frac{t}{D} = 83.037 + 0.199.p - (0.276 - 0.0025.p) \left( \frac{n. c. c.}{t} \right)$$

when  $p = 11$  to  $20$ , and  $t = 4^\circ$  to  $40^\circ$ . This would yield a value of  $81.25$  when  $p = 15$  and  $t = 20$ , whereas the formula of Meissl gives  $80.88$ , or  $81.07$  when based on Mohr's c. c. Fresh aqueous solutions of lactose show birotation, but after standing about six hours the normal rotation is obtained.

B. When the sp. rot. power of a substance is dependent upon the concentration to such a degree that the simple formula

$$c = \frac{100a}{[\alpha] l}$$

can not be used, another form of calculation is adopted. In all such cases where the variation in sp. r. power can be expressed by a linear function and the third term of the equations (3) and (4) does not appear, the %-content of a solution may be found by

$$a + b p = \frac{100a}{l d p} \text{ or } \mathfrak{A} + \mathfrak{B}c = \frac{100a}{l c},$$



whence 
$$p = -\frac{a}{2b} \pm \sqrt{\left(\frac{a}{2b}\right)^2 + \frac{100}{b} \cdot \frac{a}{1d}}, \quad (8a)$$

$$c = -\frac{\mathfrak{A}}{2\mathfrak{B}} \pm \sqrt{\left(\frac{\mathfrak{A}}{2\mathfrak{B}}\right)^2 + \frac{100}{\mathfrak{B}} \cdot \frac{a}{1}}. \quad (8b)$$

These formulas need be used only when only the formulas (3) and (4) are given for the active substance. If the data of the determination are at one's disposal, it is simpler to deduct the constants of the equation of the form

$$p = a_1 \frac{a}{1} + b_1 \left(\frac{a}{1}\right)^2. \quad (9a)$$

$$c = \mathfrak{A}_1 \frac{a}{1} + \mathfrak{B}_1 \left(\frac{a}{1}\right)^2 \quad (9b),$$

hence taking  $p$  and  $c$  direct as functions of the angular rotation. These latter equations are also applicable when the variation of the sp. rot. power are represented by a curve, and hence equations (3) and (4) appear with all three members.

For example, a number of mixtures of nicotin and alcohol are given, the rotatory power of which had been determined by the author. The rapidly diminishing rotatory power as the % of alcohol  $q$  increased is expressed by the formula

$$[\alpha] \frac{20}{D} = -160.83 + 0.2224 q,$$

which transposed for  $p$ , the value of nicotin, gives

$$[\alpha] \frac{20}{D} = -138.59 - 0.2224 \cdot p \left( \text{t. c. c. d. } \frac{20}{4} \right),$$

and by inserting the constants of the equation (8a)

$$p = +311.58 - \sqrt{97082.5 - 449.64 \frac{a}{1d}}$$

By use of formula (9b), based upon calculations and experiments\*, the following formula results

$$c = 0.704 \frac{a}{1} - 0.000525 \left(\frac{a}{1}\right)^2.$$

With these formulas very accurate determinations of nicotin

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\* Ann. Chem., (Liebig) 189, p. 320.

can be made, which suggests their use for determining the quantity of nicotin in tobacco.

In like manner the quantity of camphor in alcoholic solution may be determined.

According to the author's experiments\* the rapid increase of the sp. rot. power as the concentration increases is expressed by the formula

$$[\alpha] \frac{20}{D} = 41.982 + 0.11824 \cdot c \left( \text{t. c. c. d } \frac{20}{4} \right)$$

whence with formula (8 b) as a basis the following results,

$$c = -177.53 + \sqrt{31516.45 + 845.74 \frac{a}{l}} \quad (\text{I.})$$

From direct observations for the constants of equations (9 b) results

$$c = 2.3614 \frac{a}{l} - 0.01158 \left( \frac{a}{l} \right)^2 \quad (\text{II.})$$

In the table supplied Z. A. C. 28, p. 217, the results obtained by the use of the formulas are shown to be subject to an error of but  $-.16$  to  $+0.13$  as extremes.

Instead of the above method another may be adopted for the calculation by first inserting in

$$c = \frac{100a}{[a]l}$$

an approximate value for  $[a]$  and recalculate with the value of  $c$ , obtained from  $[a] = \mathfrak{A} + \mathfrak{B}c$ , the value  $[a]$ . The latter result is then inserted in the first formula and the recalculations repeated 4 or 5 times until  $c$  becomes a constant quantity.

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\* Ann. Chem., (Liebig) 189, p. 333.



## MICHEL EUGÈNE CHEVREUL.

1786-1889.

Michel Eugène Chevreul was born at Angers, France, August 31st, 1786, and died in Paris April 9th, 1889, at the age of 102 years, 7 months and 9 days.

His career was practically coextensive with the history of Chemistry, with which he is inseparably connected.

He was the "Doyen" of the students, as he liked to call himself.

It is a century of honor, probity and scientific labor which has descended into the grave. He died after having taken his part in the great intellectual impulse of this century and after having materially contributed to the advancement of French science, of which he was the Nestor. At his birth Chemistry, in its present sense, was practically an unknown science, the system of Lavoisier was just beginning to make headway against the Phlogiston theories of Beecher and Stahl, and the lingering remnants of Alchemy. Of all the splendid and surprising scientific achievements of the century since then, he has been an intelligent and interested witness, in many of them an important and vital factor. After having completed his course of studies at the "Ecole Centrale" of Angers, in 1803, at the age of seventeen Chevreul came to Paris and was admitted by Vauquelin as manipulator in his chemical manufactory, but soon after was made chief of the laboratory.

At that time chemical science was yet in a rudimentary state. Black's observations on lime in 1752, which led him to find what we now call carbonic acid, and to recognize that there were different kinds of air, had remained almost unnoticed, as well as Rey's and Mayow's much earlier works. In 1774 Priestley discovered a separate air which he called "Dephlogisticated air," which air or gas we now call Oxygen, according to the system of Lavoisier. These and other discoveries had given an impulse to chemical researches, and the active mind of Lavoisier, in conjunction with

the vigorous intellect of Guiton de Morveau, the mathematical power of Monge and de Laplace, and the manipulative skill of Berthollet and Fourcroy had correlated the facts, and from them elaborated the system and nomenclature which have been followed so long. Chevreul was but eight years old when Lavoisier died. The school of Lavoisier survived the death of its leader, and the time of Chevreul's arrival in Paris was that of the active spread of the spirit of experimental inquiry.

At the age of twenty, in 1806, he first published a scientific paper which bore a geological character, being a chemical examination of the fossils found in the Department of Eure and Loire.

In 1810 Vauquelin appointed him preparator to his course of applied chemistry at the Museum of Natural History, and in 1813, at the instance of his illustrious master, he was made an officer of the University and was given the chair of Chemistry at the "Lycée Charlemagne." In 1818 he was a candidate for membership at the "Académie des Sciences," but withdrew his name as candidate to allow Proust to be elected.

In 1824 he received the professorship of special chemistry at the Gobelins and succeeded Roart as director of the dye works of this establishment.

In 1826 he succeeded Proust at the "Académie des Sciences," and the same year was made a Fellow of the Royal Society of London.

In 1834 he obtained his first promotion in the "Légion d'Honneur."

In 1851 he was awarded a premium at the London industrial exhibition for the benefit his labors had conferred on industry. He was a member of the international jury at the universal exhibition of 1851, in London, and of 1855 in Paris.

He was the president of the Society of Agriculture. He had been made "Commandeur de la Légion d'Honneur" in 1844, "Grand Officer" in 1865, and "Grand-croix" January 5th, 1875.

February 10th, 1879, he resigned as director of the Museum, but still retained his professorship.

In 1886 France celebrated the jubilee of his first century, the Members of the Government entertained him at a banquet in the

"Hotel de Ville" and his statue was unveiled in the gardens of the Museum of Natural History with which he had been so long connected.

Among his numerous honorary titles, the first he received was the degree of M. D. from the University of Berlin, and the last the degree of LL.D. from the University of Glasgow, which was bestowed on him the day he reached his one hundredth year.

His funeral was conducted by the State with military honors, and among the deputations present was that of the French "Stéariniers."

In 1823 Chevreul published his "*Recherches sur les corps gras*," and showed that fats and ethers belonged to the same family; he also gave the theory of saponification obtained either by acids or by bases, and demonstrated that these agents decomposed the fatty substances by transforming them into acids and into glycerine, with the absorption of a certain number of molecules of water. The water absorbed in this transformation promotes the formation of the fatty acids and the glycerine is left free. He found that when a fatty substance is submitted to the action of a strong acid, the decomposition is instantaneous, because the acid (fatty) separates in the free state while the glycerine combines with the acid used for the decomposition. When a strong base is used it combines with the fatty acid and the glycerine is isolated.

Glycerine had been discovered in 1779 by Scheele, but it was considered as existing only accidentally in certain oils. Chevreul demonstrated that it was always separated during saponification and that fatty bodies might be considered as true salts formed by a fixed base, glycerine, and a variable acid.

The manufacture of "Bougies stéariques" or stearic candles has been a direct application derived from these researches. This industry made the fortune of numerous manufacturers, but not the fortune of the inventor nor that of Gay-Lussac who had joined Chevreul for the exploitation of the discovery. Chevreul abandoned his rights and the new industry was taken up by Demilly, of St. Denis, and to this day the products of this establishment are universally known under name of "Bougies de l'Etoile."

For this discovery Chevreul received, in 1852, the prize of

12,000 francs founded by the Marquis d'Argenteuil for the encouragement of national industry.

He was also rewarded by the Royal Society of London with the Copley medal.

In these researches on fatty bodies, oleic acid was isolated and applied in the preparation of wool for cloth.

When Chevreul was appointed director of the dye works of the Gobelins, he gave his attention to the practice of dying, which at that time depended very often upon the most complicated and unscientific recipes transmitted from father to son for generations. He introduced a process for dyeing in black; previously the black threads used in the Royal manufacture were obtained from a hat dyer who jealously guarded his process.

His works on dyeing are extensive and he divided them into three series.

1. *Physical Researches.*

The Contrast of Colors, published first in 1828 in Vol. XI. of the "Mémoires de l'Académie," completed and published in book form in 1839.

Theory of the Optical Effects of Silken Fabrics.

The Chromatic Circles.

Previous to Chevreul, Buffon (1744), the Jesuit Scherffer (1754), Épinus and Darwin (1785) and Rumford (1802) had described several phenomena relating to colors, and these facts correlated and added to his own observations enabled Chevreul to give the law of their contrast.

According to Chevreul, a substance possessing any one of the colors of the spectrum can only be modified in four different ways.

1. By white, which reduces it in intensity.
2. By black, which diminishes its specific intensity.
3. By a certain color, which changes the specific property without rendering it less bright.
4. By a certain color which changes the specific property and renders it less bright, so that if the effect is carried to the highest degree, it results in black or normal gray, represented by black mixed with white in a certain proportion.

To express all these modifications, he used the following terms, which once defined can no longer be equivocal.

The *tones* of a color are the different degrees of intensity of which this color is susceptible, according as the matter which presents it is pure or simply mixed with white or black ; the *scale*, the whole of the tones of the same color ; the *shades* of a color are the modifications which it undergoes by the addition of another color which changes it without rendering it less bright ; the *subdued scale*, the scale whose light tones as well as the dark ones are dulled by admixture with black (*couleurs rabattues*).

To construct the chromatic circles, he proceeded as follows :

Having divided a circle into seventy-two equal sections, he placed at equal distances three patterns of tinted wool, one red, another yellow, the third blue, of the same intensity of color. Between these three sections, and at an equal distance from each, he placed orange between the red and yellow, green between this latter and the blue, and violet between the blue and red. By continuing in the same manner successive intercalations and intermediate colors and shades, he at last obtained what he called a chromatic circle of "*couleurs franches*" reproducing the spectrum of solar light.

When these seventy-two shades were obtained, he took each of them to make a complete scale formed by the addition of increasing quantities of white and black, in order to have ten subdued tones and ten tones of the same color rendered clearer by white. Each scale therefore comprised, between the extremes of pure white and pure black, twenty different tones, of which the pure color is the tenth starting from white.

From this first combination there are already 1440 different tones, all deduced from the chromatic scale of pure colors, but in successively subduing the seventy-two tones of this circle by the addition of 1, 2, 3, etc., tenths, of black, nine circles of subdued colors are formed, and each of the seventy-two tones which they comprise becoming in its turn the type of a scale of twenty new ones proceeding from white to black, there follows, for the complete series, a scale of 14,400 tones, to which must be again added the twenty ones of normal gray, which makes 14,420 different tones.

## 2. *Physico-Chemical Researches.*

The blending of colors and their application as dye stuffs.



### 3. *Chemical Researches.*

In these researches published in the "Mémoires de l'Académie" from 1831 to 1836, he isolated a great number of the coloring principles of the matters used in dyeing. He studied the action of light, heat, humidity, etc., upon dyed materials. He was led to admit that the coloring matters united with tissues by a special force which he called capillary attraction. He explained how fabrics dyed with Prussian blue and exposed to the rays of light in a dry or moist vacuum, lost their blue color in giving off cyanogen or hydrocyanic acid and how they regained it when exposed in an atmosphere containing oxygen.

From these observations he deduced some general principles and considerations relative to the matter of living organized beings, and conceived the following hypothesis: "Supposing that an organized being contains Prussian blue in a liquid acting as sap or blood, and that this liquid enters an organ exposed to the action of light which could reduce the coloring principle into cyanogen and protocyanide of iron; supposing that an exhalation of cyanogen occurs, and then an absorption of oxygen; supposing this oxygen to be carried with the protocyanide of iron in organs where light has no action and where Prussian blue and peroxide of iron are formed, the exhalation of cyanogen and the discolorization of the liquid containing the Prussian blue in the organ which has been exposed to light, and the recoloration of this liquid produced by an absorption of the oxygen, are phenomena which would be explained as produced by a *vital force*, if the properties that we have described were not known; but if these properties were known, and if it were also known that a coloring matter having the characters above described was found in the liquids of a living being, it would be an easy matter to explain the discoloration and the recoloration without having recourse to a *vital force*."

Another exhaustive work of Chevreul was his analysis of wool-fat. He pointed out that this peculiar compound "Suint" formed no less than one-third of the raw merino wool from which it may be readily freed by simple immersion in cold water.

From this wool-fat he isolated several bodies which he did not

name, but represented provisionally by Greek letters. One of these was named in the following manner : One day in 1868 Chevreul was in a room containing specimens belonging to the Museum, and his attention was attracted by an odor which was similar to the smell emitted by one of his unnamed products. This odoriferous emanation came from the stuffed body of an old albatross which had been forgotten in a closet. The bird was brought to the laboratory at the Gobelins, its feathers tied in bunches with a string and placed under an inverted jar with baryta water. After a month a current of carbonic acid was passed through the baryta water, the precipitate separated by filtration and the clear liquid submitted to distillation in a glass retort. Before the boiling point of water had been reached a liquid condensed in the receiver. Upon examination it proved to possess the same properties as one of the products of wool-fat. It was a volatile acid, and having been obtained from a bird it was named Avic acid. In extracting the fatty matters from wool Chevreul remarked that ether turns acid very quickly and therefore is not well suited for this kind of investigation.

It would be a difficult task to describe fully all the works of Chevreul. The scientific publications of his time are full of the results of his observations. We will therefore give only a brief record of some of his productions.

In his researches on indigo (1812) he found that woad and other indigo bearing plants held in their sap indigo white, which contains one molecule more of hydrogen than indigo blue. This indigo white is transformed by oxidation or exposure to air into indigo blue. He gave the composition of butter, showing that it is a compound of glycerides, among which he noted stearin and olein, and the combinations of butyric, caproic and capric acid with glycerine. He found that some salts formed by the union of a weak acid with alkalies are decomposed by water, and acid salt is precipitated and a portion of the alkali left in solution (Sodium stearate.)

He found that when spermaceti or cetin is saponified no glycerine is produced, but instead a matter which he named Ethal.

He discovered delphinic or phocenic acid (1817) in the oil of

*Delphinus Phocæna*, which acid proved to be the same as valerianic acid, obtained later from valerian.

He extracted hircic acid from the fat of the goat (*Hircus*).

He obtained sebacic acid from the distillation of oleic acid, and Butyral from the dry distillation of calcium butyrate.

He discovered that linseed oil could be rendered siccative by manganese oxide at a comparatively low temperature, thus giving a product much lighter in color than when litharge is used. He also suggested the use of oxide of zinc, instead of oxide of lead, for white paint.

Fourcroy thought that cholesterin and spermaceti were the same substance. Chevreul showed that it is a distinct product, made its analysis, described its properties and named it.

He gave the analysis and composition of adipocire.

He obtained creatin (1832) by treating with alcohol the residue from evaporation (in vacuo) of bouillon.

From cork he obtained suberin.

From nutgalls he obtained ellagic acid.

He found that when calcium sulphate is in contact in the dark with moist organic matter, it was transformed first into calcium sulphide, and later into hydrogen sulphide, and also demonstrated that the emanations produced when the ground is open in the vicinity of gas mains were not entirely due to a leakage of gas.

He showed that grape sugar has the same composition as diabetic sugar.

He gave a method for separating zirconium from iron founded on the difference of solubility of their chlorides in hydrochloric acid.

Another work of his, on sanitary influences, introduced the practice of charring the interior of water casks. In collaboration with Magendie, he gave the composition of intestinal gases.

It is to him that the methods of fractional distillation and fractional precipitation are due.

In 1885 he completed his studies on colors, and his observations on colors in motion were published in the "Mémoires de l'Académie."

His definition of chemistry, "*La chimie est la science qui réduit la matière à des espèces qui sont caractérisées par leurs propriétés.*"

He has published numerous works, among which are :

Leçons de Chimie appliquée à la Teinture, 1828-31.

De la loi du Contrast Simultané des Couleurs, 1839.

Essai de mécanique Chimique, 1854.

De la baguette divinatoire, 1854.

Considérations sur l'histoire de la partie de la Medecine qui concerne la prescription des remèdes, 1865.

Histoire des connaissances Chimique, 1866.

It would seem as if the amount of laboratory work performed by Chevreul would have required all his time, but indefatigable worker as he was, his moments of leisure, as he called them, were turned towards philosophy. A true friend of Truth, he only published his results after he had probed them with the severest criticism. He had borrowed his motto from Mallebranche, "*On doit tendre avec effort à l'infailibilité sans y prétendre*," and he never departed from it.

Studying and learning constantly he had acquired such a proficiency in the different branches of human knowledge that he has been surnamed "*Encyclopédie vivante*." He did not like to be called a savant, and among all the distinctions and titles that he had received he said that the one he cherished the most was that of "*Doyen des Etudiants*."

A monument was erected to Chevreul during his lifetime, but a more lasting tribute to his memory, one which would be coveted by any man of science, would be the publication of his complete works.

A. BOURGOUGNON,

Formerly assistant at the

"Manufacture Nationale des Gobelins."

# POLARISTROBOMETRIC-CHEMICAL ANALYSIS.

BY H. LANDOLT.

(Concluded.)

Translated by J. F. Geisler.

(*Ztschr. anal. Chem.*, 28, 203-234.)

## II.

### *Solutions of one active substance in two inactive solvents.*

As is well known, the specific rotatory power of optically active substances is unequally affected by different solvents. If the individual action of two solvents is expressed by  $[a] = A + Bq$  and  $[a]_1 = A + B_1 q_1$ , in which the constants A, representing the specific rotatory power of the pure active substance, must agree, then if q and  $q_1$  express the parts by weight in 100 parts by weight of the solution, the equation may be expressed by

$$[a]_m = A + Bq + B_1 q_1 \quad (10).$$

It would be taken for granted that each of the solvents in the mixture would have the same effect as if used alone. This is generally not to be expected, since, as is also indicated by changes in the density of mixed solvents, a physical change takes place in the molecules, thus causing a different effect upon the active substance. If this effect is but slight, the value of  $[a]_m$  will be between  $[a]$  and  $[a]_1$  and can then be determined more or less closely by the above formula. It may happen, however, that the mixture causes an altogether different effect, and may possibly increase the rotatory power above that of either of the solvents, in which case a maximum must result from a given mixture of the solvents.

As an example of the first instance, the behavior of narcotin, as observed by Hesse\* in using about equal concentrations ( $c = 0.74$  to 2), is cited:

Solution in alcohol of 97 vol. %	$[a]_D = -185.0$
“ “ chloroform	$[a]_D = -207.4$
Solution in mixture of 1 vol.	
of alcohol and 2 vols.	
chloroform .....	$[a]_D = -191.5$

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\* Ann. Chem. (Liebig), 176, p. 192.

An increase in the rotatory power by the use of mixed solvents is shown in the following instances:

According to Hesse,\* cinchonidine gives for a concentration of  $c = 2$ .

When dissolved in alcohol of 97% vol.  $[a]_D = -106.9$

“ “ “ chloroform  $[a]_D = -83.9$

When dissolved in alcohol-chloroform

(1:2) .....  $[a]_D = -108.9$

For dry cinchonidine nitrate and hydrochloride Oudemant† obtained:

	Nitrate.	Hydrochloride.
Solvent.....c =	1.855	c = 1.722
Water ..... $[a]_D =$	99.9	— 99.9
Absolute alcohol..... $[a]_D =$	103.2	— 104.6
80% (wt.) alcohol +		
20% water..... $[a]_D =$	127.0	— 128.7
89% (wt.) alcohol +		
11% water ..... $[a]_D =$	119.0	— 119.6

Quinidine hydrochloride shows, according to Oudemant, for a concentration of 1.89 of the dried salt

Dissolved in water.....	$[a]_D = +190.8$
“ “ absolute alcohol.....	$[a]_D = 199.4$
“ “ alcohol 90.5% (by wt.).....	$[a]_D = 213.0$

In solutions of quinine hydrochloride ( $2H_2O$ ) Hesse‡ found that in mixtures of alcohol and water (vol. %) the maximum rotation occurs with a concentration

of  $c = 2$ , when the vol. % of water  $q = 60$

q=0 (water)	20	40	50	60	70	80	85	90	97
$[a]_D =$	—138.8	166.6	182.8	187.5	187.8	182.3	174.8	168.3	160.8 143.9

For the sp. rot. power of cinchonine in mixtures of chloroform and alcohol Oudemant§ gives the following:

\* Ann. Chem. (Liebig), 176, p. 219.

† Ann. Chem. (Liebig), 182, p. 49, 50.

‡ Ann. Chem. (Liebig), 176, p. 210.

§ Schiebler, Neue Ztschr. f. Rüb. Ind., III., p. 180.

	1	2	3	4	5	6	7	8	9	10	11
Chloroform,	100.00	99.66	98.74	94.48	86.95	82.26	65.00	44.29	27.54	17.02	0.00
Alcohol,	0.00	0.34	1.26	5.52	13.05	17.74	35.00	55.71	72.46	82.98	100.00
$[\alpha]_D = +$	212.0	216.3	226.4	236.6	237.0	234.7	229.5	226.6	227.6	227.8	228.0

Here the maximum rotation is observed when the mixture contains 10% of alcohol. This shows, moreover, that in an alcoholic solution of cinchonine, fully one-half of the alcohol could be replaced by chloroform without causing any great difference in the angular rotation, whereas in a chloroform solution of the alkaloid the mere replacement of  $\frac{1}{3}$  of the chloroform by alcohol would cause an increase of about  $4^\circ$ .

Hence the determination of the angular rotation by such a mixed solvent is only practicable when the proportions of the mixed solvents remain constant, so that it will act as a homogeneous solution. Hesse used, mostly, a solution composed of 1 vol. alcohol of 97% by vol. and 2 vols. of chloroform as a solvent for alkaloids. Cane sugar seems to be about the only substance whose rotatory power is not affected by mixed solvents. According to Seyferth,\* the angular rotation for cane sugar in varying mixtures of alcohol and water is practically constant, whereas Tollens† found that alcohol slightly increased the angular rotation, also methyl alcohol and acetone to a somewhat greater extent. Thus for 10% solutions of cane sugar in mixtures composed of 3 parts by vol. of the above solvents and 1 part by vol. of water, Tollens found the rotatory power to be:

In water solution.....	$[\alpha]_D = 66.667$
Water and alcohol.....	$[\alpha]_D = 66.827$
Acetone and water.....	$[\alpha]_D = 67.396$
Methyl, alcohol and water.....	$[\alpha]_D = 68.628$

The above conditions may arise when solutions of an active substance consist of but one solvent, but contain also one or more inactive substances. In such cases the effect of the latter must be determined by experiment.

### III.

#### *Solutions of two active substances in one inactive solvent.*

Under these conditions the solvent may affect the specific

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\* Ann. Chem. (Liebig), 169, p. 71.

† Ber. d. chem. Ges., 1880, p. 2297.

rotatory power of each of the active substances and these latter, moreover, affect each other. A quantitative determination of the two substances is then possible only when the variation is so small that the angular rotations may be considered as constant for the concentration limits.

The method of analysis will depend upon whether the combined weight of the two substances is known or not.

A. The compound is a solid consisting of two optically active substances.

Weigh out  $g$  grms. of the compound, dissolve and dilute to 100 c.c., determine the angular rotation  $a$  in a 1 dm. tube, and calculate from this the specific rotatory power

$$[a] = \frac{100a}{l \cdot g}.$$

If the mixture contain  $X\%$  of a substance of which the spec. rot. pow. is  $[a]_x$  and  $y = 100 - x$  per cent. of the other substance with the sp. rot. pow.  $[a]_y$ , then

$$[a]_x \cdot X + [a]_y (100 - X) = 100 [a], \text{ whence}$$

$$X = 100 \frac{[a] - [a]_y}{[a]_x - [a]_y},$$

$$y = 100 - X = 100 \frac{[a] + - [a]}{[a] + - a]_y} \quad (11)$$

As an example, several mixtures of cane sugar and raffinose are given for which Clerget\* found the degrees by Ventzke's scale and by multiplying by 0.3465 calculated the angular degrees.

	In 100 c. c. 20 g of a mixture.		Observed deviation for 1 dm. tube 1 — 2 dm.		Spec. rot. of the mixture. [a]
	Cane Sugar.	Raffinose.	Ventzke.	Ang. degrees $a_D$	
I.	16 g	4 g	+85.45	+29.608	+74.02
II.	17 g	3 "	83.45	28.915	72.29
III.	18 g	2 "	81.13	28.112	70.28
IV.	19 g	1 "	79.00	27.374	68.43

\* Z. V. f. R. Z. I., 1887, 153.



Taking the following rotations as constants

Cane sugar,  $[a]_D = + 66.5 = [a]_x$

Raffinose,  $[a]_D = + 104.5 = [a]_y$

Then the % of cane by the formula would be

	I.	II.	III.	IV.
	80.21	84.76	90.05	94.92 %
instead of	80.	85.	90.	95. %

If the calculation were to be made with Ventzke's degrees then the given rot. power for cane sugar and raffinose would have to be divided by 0.3465.

If the sp. rotation of the respective substances may not be considered constant, but the variation is known through the equation  $[a] = A + Bc$ , calculate from the values which are nearest those for the concentration used, and then substitute them in equation (11). In this manner Hesse\*\* effected the analysis of various mixtures of alkaloids and their salts, of which the following is cited :

A mixture of quinine sulphate ( $C_{20}H_{24}N_2O_8 \cdot H_2SO_4 + 7H_2O$ ) and cinchonine sulphate ( $C_{20}H_{24}N_2O_8 \cdot H_2SO_4 + 4H_2O$ ), for a solution of 4 grms. of the same per 100 c. c., showed a specific rotation of  $[a]_D = - 71.87$ .

For the individual salts the sp. rotation was found to be affected by the concentration of the aqueous solution as follows :

Quinine sulphate  $[a]_D = - 164.85 + 0.31.c$ .

Cinchonine "  $[a]_D = + 212.0 - 0.8.c$ .

If it be taken for granted that the two constituents are present in equal proportions for each  $c = 2$ , then according to equation (11) the % of quinine sulphate in the mixture is

$$\frac{- 71.81 - 210.4}{-164.23 - 210.4} = 75.3\% \text{ as against } 75.\%$$

the amount really present.

The uncertainties which might arise through the value of  $c$  are avoided by working with low concentrations.

B. The combined weight of the two active substances is not known, and either the number of grammes of the same in 100 c.c. of solution, or their % in a solid substance is to be ascertained.

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\*\* Ann. Chem. (Liebig), 182, 148.

Under these conditions the analysis can often be accomplished by determining first the angular rotation of the original solution, and again after one, or both, of the active substances has been converted by chemical agents into a new active body. The method was first applied by Clerget in the analysis of mixtures of cane sugar and invert sugar, and is known as the Inversion method.

The two cases are the following :

(a.) By the chemical reaction only one of the two substances is converted into a new active compound, while the other remains unchanged.

Representing by  $c_1$  and  $c_{11}$  the unknown concentrations of the two substances, and  $[a]_1$  and  $[a]_{11}$  their rotatory power,

$[a]_{111}$  the sp. rotation of the product of the inversion,

$k$  the quantity of the chemical equivalent which one part by weight of the changeable substance will yield,

$a$ , the observed angular rotation of the original solution,

$a_1$ , the angular rotation after the inversion,

$l$ , the length of the tubes in decimeters,

Then the following two equations express the conditions before and after inversion, when the factors  $[a]_{111}$  and  $k$  are based on the spec. rotation  $[a]_1$ ,

$$[a]_1 c_1 + [a]_{11} c_{11} = \frac{100. a}{l (c_1 + c_{11})} (c_1 + c_{11}),$$

$$[a]_{111} k c_1 + [a]_{11} c_{11} = \frac{100. a_1}{l (k c_1 + c_{11})} (k c_1 + c_{11}),$$

whence

$$\begin{aligned} c_1 &= \frac{100 (a - a_1)}{l ([a]_1 - [a]_{111} k)}, \\ c_{11} &= \frac{100 ([a]_1 a_1 - [a]_{111} k a)}{l [a]_{11} ([a]_1 - [a]_{111} k)}. \end{aligned} \quad (12)$$

The calculation can also be made in the following manner :  
From the specific rotation of each of the substances find by the formula

$$a = \frac{[a] l c}{100}$$

the angular rotation of a solution of the concentration in a tube of a given length (2 dm.)

Representing by

$\varphi_1$  and  $\varphi_{11}$  the angular rotations as found for the two substances,

$\rho$  the angular rotation of the inverted substance,

then, having calculated all the angular rotations for tubes of the same length, we have

$$\text{Before the inversion, } \varphi_1 c_1 + \varphi_{11} c_{11} = a,$$

$$\text{After " " } \rho k c_1 + \varphi_{11} c_{11} = a_1,$$

which lead to the formulas

$$c_1 = \frac{a - a_1}{\varphi_1 - \rho k},$$

$$c_{11} = \frac{\varphi_1 a_1 - \rho k a}{\varphi_{11} (\varphi_1 - \rho k)} \text{ or } = \frac{a - \varphi_1 c_1}{\varphi_{11}}. \quad (13)$$

If the specific rotations of the respective substances and hence, also the angular rotations  $\varphi_1$   $\varphi_{11}$   $\rho$  are not constant, the concentrations  $c_1$  and  $c_{11}$  must first be ascertained by means of medium values, and then the necessary figures from  $[a] = \mathbf{A} + \mathbf{B}c$  inserted in the above equations.

When the specific rotation of the inverted product is unknown, where possibly the product is a mixture of several substances, the angular rotation of a definite quantity of the original substance after inversion, must first be ascertained by preliminary trials. This angle, calculated for the concentration of 1 grm. in 100 c.c., represents the product  $\rho k$  and must be inserted in place of the same in the formula (13). If the angle is variable then it must be ascertained for various concentrations of the original active substance. Concerning the practical application of the method, it must be borne in mind that in the chemical treatment the added reagents change the concentration of the substances, so that after the reaction the solution must be diluted to a definite volume, to which volume the solution before the inversion should also be diluted and then polarized, so as to have the conditions as to concentration as near alike as possible.

As an example of the above the well-known Clerget's method for the determination of cane sugar in presence of invert sugar is given. The angular rotation  $\alpha$  is first found for the original solution, 50 c. c., then inverted, after the addition of 5 c. c. conc. hydrochloric acid, by heating for 15 min. at 67-70°, whereby all cane sugar is changed to invert sugar, and after cooling the angular rotation observed for  $\alpha_1$  making allowance\* for the dilution.

The temperature of the solutions should be kept as near 20° as possible for the polarizations. Taking for granted that for the trials a polaristrometer with Na — light and tubes of 2 dm. length were used, the following factors may be inserted in formulas (12) and (13):

$[\alpha]_1 = +66.5$  as spec. rot.  $[\alpha]_D$  of cane sugar, whence  $\varphi_1 = +1.33$  as the angular rotation, which 1 grm. of sugar in 100 c. c. would exert in a 2 dm. tube.

$[\alpha]_{11} = -20.0$  as medium spec. rot.  $[\alpha]_D$  of invert sugar in dilute solutions at 20°. Whence  $\varphi_{11} = -0.4$  for the angular rot. of 1 g in 2 dm. tube.  $k = 1.0526$ , *i. e.* the number of grammes of invert sugar which 1 grm. of cane sugar will yield according to the equation  $C_{12}H_{22}O_{11} + H_2O = 2 C_6H_{12}O_6$ .

$[\alpha]_{111}$  under these conditions  $= [\alpha]_{11}$ , and  $\rho = \varphi_{11}$ .

Finally the difference  $\alpha - \alpha_1$  becomes the sum  $S$  of the two observed angular rotations, when as is generally the case, the solution was dextro-rotatory before and lævo-rotatory after the inversion. With these constants there result for the calculation of the number of grammes of cane sugar  $c_1 = r$  and invert sugar  $c_{11} = i$  in 100 c. c. of the original solution the formulas:

$$r = \frac{\alpha - \alpha_1}{1.75} = 0.5714 S = \frac{4S}{7},$$

$$i = -0.6015. \alpha - 1.9. \alpha_1 = \frac{\alpha - 1.33 r}{-0.4}.$$

The % of invert sugar obtained by the above formula is usually

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\* (In saccharimetry this allowance is, in a measure, met by using 1.1 or 2.2 dm. tubes for the polarization of the inverted solution.) J. F. G.

*Dolphinus Phocaena*, which acid proved to be the same as valerianic acid, obtained later from valerian.

He extracted hircic acid from the fat of the goat (*Hircus*).

He obtained sebacic acid from the distillation of oleic acid, and Butyral from the dry distillation of calcium butyrate.

He discovered that linseed oil could be rendered siccative by manganese oxide at a comparatively low temperature, thus giving a product much lighter in color than when litharge is used. He also suggested the use of oxide of zinc, instead of oxide of lead, for white paint.

Fourcroy thought that cholesterin and spermaceti were the same substance. Chevreul showed that it is a distinct product, made its analysis, described its properties and named it.

He gave the analysis and composition of adipocire.

He obtained creatin (1832) by treating with alcohol the residue from evaporation (in vacuo) of bouillon.

From cork he obtained suberin.

From nutgalls he obtained ellagic acid.

He found that when calcium sulphate is in contact in the dark with moist organic matter, it was transformed first into calcium sulphide, and later into hydrogen sulphide, and also demonstrated that the emanations produced when the ground is open in the vicinity of gas mains were not entirely due to a leakage of gas.

He showed that grape sugar has the same composition as diabetic sugar.

He gave a method for separating zirconium from iron founded on the difference of solubility of their chlorides in hydrochloric acid.

Another work of his, on sanitary influences, introduced the practice of charring the interior of water casks. In collaboration with Magendie, he gave the composition of intestinal gases.

It is to him that the methods of fractional distillation and fractional precipitation are due.

In 1885 he completed his studies on colors, and his observations on colors in motion were published in the "Mémoires de l'Académie."

His definition of chemistry, "*La chimie est la science qui réduit la matière à des espèces qui sont caractérisées par leurs propriétés.*"

He has published numerous works, among which are :

Leçons de Chimie appliquée à la Teinture, 1828-31.

De la loi du Contrast Simultané des Couleurs, 1839.

Essai de mécanique Chimique, 1854.

De la baguette divinatoire, 1854.

Considérations sur l'histoire de la partie de la Medecine qui concerne la prescription des remèdes, 1865.

Histoire des connaissances Chimique, 1866.

It would seem as if the amount of laboratory work performed by Chevreul would have required all his time, but indefatigable worker as he was, his moments of leisure, as he called them, were turned towards philosophy. A true friend of Truth, he only published his results after he had probed them with the severest criticism. He had borrowed his motto from Mallebranche, "*On doit tendre avec effort à l'infailibilité sans y prétendre*," and he never departed from it.

Studying and learning constantly he had acquired such a proficiency in the different branches of human knowledge that he has been surnamed "*Encyclopédie vivante*." He did not like to be called a savant, and among all the distinctions and titles that he had received he said that the one he cherished the most was that of "*Doyen des Etudiants*."

A monument was erected to Chevreul during his lifetime, but a more lasting tribute to his memory, one which would be coveted by any man of science, would be the publication of his complete works.

A. BOURGOUGNON,

Formerly assistant at the

"Manufacture Nationale des Gobelins."

# POLARISTROBOMETRIC-CHEMICAL ANALYSIS.

BY H. LANDOLT.

(Concluded.)

Translated by J. F. Geisler.

(*Ztschr. anal. Chem.*, 28, 203-234.)

## II.

### *Solutions of one active substance in two inactive solvents.*

As is well known, the specific rotatory power of optically active substances is unequally affected by different solvents. If the individual action of two solvents is expressed by  $[a] = A + Bq$  and  $[a]_1 = A + B_1 q_1$ , in which the constants A, representing the specific rotatory power of the pure active substance, must agree, then if q and  $q_1$  express the parts by weight in 100 parts by weight of the solution, the equation may be expressed by

$$[a]_m = A + Bq + B_1 q_1 \quad (10).$$

It would be taken for granted that each of the solvents in the mixture would have the same effect as if used alone. This is generally not to be expected, since, as is also indicated by changes in the density of mixed solvents, a physical change takes place in the molecules, thus causing a different effect upon the active substance. If this effect is but slight, the value of  $[a]_m$  will be between  $[a]$  and  $[a]_1$  and can then be determined more or less closely by the above formula. It may happen, however, that the mixture causes an altogether different effect, and may possibly increase the rotatory power above that of either of the solvents, in which case a maximum must result from a given mixture of the solvents.

As an example of the first instance, the behavior of narcotin, as observed by Hesse\* in using about equal concentrations ( $c = 0.74$  to 2), is cited:

Solution in alcohol of 97 vol. %	$[a]_D = -185.0$
“ “ chloroform	$[a]_D = -207.4$
Solution in mixture of 1 vol.	
of alcohol and 2 vols.	
chloroform .....	$[a]_D = -191.5$

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\* Ann. Chem. (Liebig), 176, p. 192.

An increase in the rotatory power by the use of mixed solvents is shown in the following instances:

According to Hesse,\* cinchonidine gives for a concentration of  $c = 2$ .

When dissolved in alcohol of 97% vol.  $[a]_D = -106.9$

“ “ “ chloroform  $[a]_D = -83.9$

When dissolved in alcohol-chloroform

(1:2) .....  $[a]_D = -108.9$

For dry cinchonidine nitrate and hydrochloride Oudemant† obtained:

	Nitrate.	Hydrochloride.
Solvent.....c =	1.855	c = 1.722
Water ..... $[a]_D =$	99.9	— 99.9
Absolute alcohol..... $[a]_D =$	103.2	— 104.6
80% (wt.) alcohol +		
20% water..... $[a]_D =$	127.0	— 128.7
89% (wt.) alcohol +		
11% water ..... $[a]_D =$	119.0	— 119.6

Quinidine hydrochloride shows, according to Oudemant, for a concentration of 1.89 of the dried salt

Dissolved in water.....	$[a]_D = +190.8$
“ “ absolute alcohol.....	$[a]_D = 199.4$
“ “ alcohol 90.5% (by wt.).....	$[a]_D = 213.0$

In solutions of quinine hydrochloride ( $2H_2O$ ) Hesse‡ found that in mixtures of alcohol and water (vol. %) the maximum rotation occurs with a concentration

of  $c = 2$ , when the vol. % of water  $q = 60$

q=0 (water)	20	40	50	60	70	80	85	90	97
$[a]_D =$	—138.8	166.6	182.8	187.5	187.8	182.3	174.8	168.8	160.8 143.9

For the sp. rot. power of cinchonine in mixtures of chloroform and alcohol Oudemant§ gives the following:

\* Ann. Chem. (Liebig), 176, p. 219.

† Ann. Chem. (Liebig), 182, p. 49, 50.

‡ Ann. Chem. (Liebig), 176, p. 210.

§ Schiebler, Neue Ztschr. f. Rüb. Ind., III., p. 180.



	1	2	3	4	5	6	7	8	9	10	11
Chloroform,	100.00	99.66	98.74	94.48	86.95	82.26	65.00	44.29	27.54	17.02	0.00
Alcohol,	0.00	0.34	1.26	5.52	13.05	17.74	35.00	55.71	72.46	82.98	100.00
$[\alpha]_D = +$	212.0	216.3	226.4	236.6	237.0	234.7	229.5	226.6	227.6	227.8	228.0

Here the maximum rotation is observed when the mixture contains 10% of alcohol. This shows, moreover, that in an alcoholic solution of cinchonine, fully one-half of the alcohol could be replaced by chloroform without causing any great difference in the angular rotation, whereas in a chloroform solution of the alkaloid the mere replacement of  $\frac{1}{30}$  of the chloroform by alcohol would cause an increase of about  $4^\circ$ .

Hence the determination of the angular rotation by such a mixed solvent is only practicable when the proportions of the mixed solvents remain constant, so that it will act as a homogeneous solution. Hesse used, mostly, a solution composed of 1 vol. alcohol of 97% by vol. and 2 vols. of chloroform as a solvent for alkaloids. Cane sugar seems to be about the only substance whose rotatory power is not affected by mixed solvents. According to Seyferth,\* the angular rotation for cane sugar in varying mixtures of alcohol and water is practically constant, whereas Tollens† found that alcohol slightly increased the angular rotation, also methyl alcohol and acetone to a somewhat greater extent. Thus for 10% solutions of cane sugar in mixtures composed of 3 parts by vol. of the above solvents and 1 part by vol. of water, Tollens found the rotatory power to be:

In water solution.....	$[\alpha]_D = 66.667$
Water and alcohol.....	$[\alpha]_D = 66.827$
Acetone and water.....	$[\alpha]_D = 67.396$
Methyl, alcohol and water.....	$[\alpha]_D = 68.628$

The above conditions may arise when solutions of an active substance consist of but one solvent, but contain also one or more inactive substances. In such cases the effect of the latter must be determined by experiment.

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rotatory power of each of the active substances and these latter, moreover, affect each other. A quantitative determination of the two substances is then possible only when the variation is so small that the angular rotations may be considered as constant for the concentration limits.

The method of analysis will depend upon whether the combined weight of the two substances is known or not.

A. The compound is a solid consisting of two optically active substances.

Weigh out  $g$  grms. of the compound, dissolve and dilute to 100 c.c., determine the angular rotation  $a$  in a 1 dm. tube, and calculate from this the specific rotatory power

$$[a] = \frac{100a}{l \cdot g}.$$

If the mixture contain  $X\%$  of a substance of which the spec. rot. pow. is  $[a]_x$  and  $y = 100 - x$  per cent. of the other substance with the sp. rot. pow.  $[a]_y$ , then

$$[a]_x \cdot X + [a]_y (100 - X) = 100 [a], \text{ whence}$$

$$X = 100 \frac{[a] - [a]_y}{[a]_x - [a]_y},$$

$$y = 100 - X = 100 \frac{[a] + - [a]}{[a] + - a}_y \quad (11)$$

As an example, several mixtures of cane sugar and raffinose are given for which Clerget\* found the degrees by Ventzke's scale and by multiplying by 0.3465 calculated the angular degrees.

	In 100 c. c. 20 g of a mixture.		Observed deviation for 1 dm. tube 1 — 2 dm.		Spec. rot. of the mixture. [a]
	Cane Sugar.	Raffinose.	Ventzke.	Ang. degrees $a_D$	
I.	16 g	4 g	+85.45	+29.608	+74.02
II.	17 g	3 "	83.45	28.915	72.29
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Taking the following rotations as constants

Cane sugar,  $[a]_D = + 66.5 = [a]_x$

Raffinose,  $[a]_D = + 104.5 = [a]_y$

Then the % of cane by the formula would be

	I.	II.	III.	IV.
	80.21	84.76	90.05	94.92 %
instead of	80.	85.	90.	95. %

If the calculation were to be made with Ventzke's degrees then the given rot. power for cane sugar and raffinose would have to be divided by 0.3465.

If the sp. rotation of the respective substances may not be considered constant, but the variation is known through the equation  $[a] = A + Bc$ , calculate from the values which are nearest those for the concentration used, and then substitute them in equation (11). In this manner Hesse\*\* effected the analysis of various mixtures of alkaloids and their salts, of which the following is cited :

A mixture of quinine sulphate ( $C_{20}H_{24}N_2O_2 \cdot H_2SO_4 + 7H_2O$ ) and cinchonine sulphate ( $C_{20}H_{24}N_2O_2 \cdot H_2SO_4 + 4H_2O$ ), for a solution of 4 grms. of the same per 100 c. c., showed a specific rotation of  $[a]_D = - 71.87$ .

For the individual salts the sp. rotation was found to be affected by the concentration of the aqueous solution as follows :

Quinine sulphate  $[a]_D = - 164.85 + 0.31.c$ .

Cinchonine "  $[a]_D = + 212.0 - 0.8.c$ .

If it be taken for granted that the two constituents are present in equal proportions for each  $c = 2$ , then according to equation (11) the % of quinine sulphate in the mixture is

$$\frac{- 71.81 - 210.4}{-164.23 - 210.4} = 75.3\% \text{ as against } 75.\%$$

the amount really present.

The uncertainties which might arise through the value of  $c$  are avoided by working with low concentrations.

B. The combined weight of the two active substances is not known, and either the number of grammes of the same in 100 c.c. of solution, or their % in a solid substance is to be ascertained.

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Under these conditions the analysis can often be accomplished by determining first the angular rotation of the original solution, and again after one, or both, of the active substances has been converted by chemical agents into a new active body. The method was first applied by Clerget in the analysis of mixtures of cane sugar and invert sugar, and is known as the Inversion method.

The two cases are the following :

(a.) By the chemical reaction only one of the two substances is converted into a new active compound, while the other remains unchanged.

Representing by  $c_1$  and  $c_{11}$  the unknown concentrations of the two substances, and  $[a]_1$  and  $[a]_{11}$  their rotatory power,

$[a]_{111}$  the sp. rotation of the product of the inversion,

$k$  the quantity of the chemical equivalent which one part by weight of the changeable substance will yield,

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Then the following two equations express the conditions before and after inversion, when the factors  $[a]_{111}$  and  $k$  are based on the spec. rotation  $[a]_1$ ,

$$[a]_1 c_1 + [a]_{11} c_{11} = \frac{100. a}{l (c_1 + c_{11})} (c_1 + c_{11}),$$

$$[a]_{111} k c_1 + [a]_{11} c_{11} = \frac{100. a_1}{l (k c_1 + c_{11})} (k c_1 + c_{11}),$$

whence

$$c_1 = \frac{100 (a - a_1)}{l ([a]_1 - [a]_{111} k)}, \quad (12)$$

$$c_{11} = \frac{100 ([a]_1 a_1 - [a]_{111} k a)}{l [a]_{11} ([a]_1 - [a]_{111} k)}.$$

The calculation can also be made in the following manner :  
From the specific rotation of each of the substances find by the formula

$$a = \frac{[a] l c}{100}$$

the angular rotation of a solution of the concentration in a tube of a given length (2 dm.)

Representing by

$\varphi_1$  and  $\varphi_{11}$  the angular rotations as found for the two substances,

$\rho$  the angular rotation of the inverted substance, then, having calculated all the angular rotations for tubes of the same length, we have

$$\text{Before the inversion, } \varphi_1 c_1 + \varphi_{11} c_{11} = a,$$

$$\text{After " " } \rho k c_1 + \varphi_{11} c_{11} = a_1,$$

which lead to the formulas

$$c_1 = \frac{a - a_1}{\varphi_1 - \rho k},$$

$$c_{11} = \frac{\varphi_1 a_1 - \rho k a}{\varphi_{11} (\varphi_1 - \rho k)} \text{ or } = \frac{a - \varphi_1 c_1}{\varphi_{11}}. \quad (13)$$

If the specific rotations of the respective substances and hence, also the angular rotations  $\varphi_1$   $\varphi_{11}$   $\rho$  are not constant, the concentrations  $c_1$  and  $c_{11}$  must first be ascertained by means of medium values, and then the necessary figures from  $[a] = \mathbf{A} + \mathbf{B}c$  inserted in the above equations.

When the specific rotation of the inverted product is unknown, where possibly the product is a mixture of several substances, the angular rotation of a definite quantity of the original substance after inversion, must first be ascertained by preliminary trials. This angle, calculated for the concentration of 1 grm. in 100 c.c., represents the product  $\rho k$  and must be inserted in place of the same in the formula (13). If the angle is variable then it must be ascertained for various concentrations of the original active substance. Concerning the practical application of the method, it must be borne in mind that in the chemical treatment the added reagents change the concentration of the substances, so that after the reaction the solution must be diluted to a definite volume, to which volume the solution before the inversion should also be diluted and then polarized, so as to have the conditions as to concentration as near alike as possible.

As an example of the above the well-known Clerget's method for the determination of cane sugar in presence of invert sugar is given. The angular rotation  $a$  is first found for the original solution, 50 c. c., then inverted, after the addition of 5 c. c. conc. hydrochloric acid, by heating for 15 min. at 67-70°, whereby all cane sugar is changed to invert sugar, and after cooling the angular rotation observed for  $a_1$  making allowance\* for the dilution.

The temperature of the solutions should be kept as near 20° as possible for the polarizations. Taking for granted that for the trials a polaristobometer with Na— light and tubes of 2 dm. length were used, the following factors may be inserted in formulas (12) and (13):

$[a]_1 = +66.5$  as spec. rot.  $[a]_D$  of cane sugar, whence  $\varphi_1 = +1.33$  as the angular rotation, which 1 grm. of sugar in 100 c. c. would exert in a 2 dm. tube.

$[a]_{11} = -20.0$  as medium spec. rot.  $[a]_D$  of invert sugar in dilute solutions at 20°. Whence  $\varphi_{11} = -0.4$  for the angular rot. of 1 g in 2 dm. tube.  $k = 1.0526$ , *i. e.* the number of grammes of invert sugar which 1 grm. of cane sugar will yield according to the equation  $C_{12}H_{22}O_{11} + H_2O = 2 C_6H_{12}O_6$ .

$[a]_{111}$  under these conditions  $= [a]_{11}$ , and  $\rho = \varphi_{11}$ .

Finally the difference  $a - a_1$  becomes the sum  $S$  of the two observed angular rotations, when as is generally the case, the solution was dextro-rotatory before and lævo-rotatory after the inversion. With these constants there result for the calculation of the number of grammes of cane sugar  $c_1 = r$  and invert sugar  $c_{11} = i$  in 100 c. c. of the original solution the formulas:

$$r = \frac{a - a_1}{1.75} = 0.5714 S = \frac{4S}{7},$$

$$i = -0.6015. a - 1.9. a_1 = \frac{a - 1.33 r}{-0.4}.$$

The % of invert sugar obtained by the above formula is usually

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\* (In saccharimetry this allowance is, in a measure, met by using 1.1 or 2.2 dm. tubes for the polarization of the inverted solution.) J. F. G.

a trifle too high (from +0.07 to +55% as shown by tables in the orig. article). Better results are obtained by the formula

$$i = -0.6005 a - 1.8729 a_1.$$

For cane sugar close results are obtained by the formula

$$r = \frac{4S}{\gamma}.$$

If a quartz-wedge saccharimeter with a Soleil or Ventzke's scale be employed for the inversion method, the following should be observed: According to the original investigations of Clerget an invert sugar solution prepared from 16.35 g cane sugar in 100 c. c. should cause a lævo-rotation of 44 degrees at 0° on the scale of a Soleil instrument, and to diminish  $\frac{1}{2}$  degree for each 1 degree rise in temperature. From this Clerget obtained the formula

$$R = \frac{100 S}{144 - \frac{1}{2} t},$$

which gives the % of cane sugar in the original substance when 16.35 (according to later statements 16.192g) of the latter are used for the Soleil or 26.048g for the Ventske saccharimeter. At the temperature 20° the normal solutions would have to polarize -34° after inversion. Later researches, however, of Creydt\* and Dr. Rathgen give us an average -32.4, whence the corrected Clerget's formula becomes

$$R = \frac{100 S}{142.4 - \frac{1}{2} t}.$$

In the technical examination of cane sugars and molasses the inversion method is subject to uncertainties, since the nature of the invert sugar may not be known,† which as already mentioned may show considerable variation in its rotatory power. In such a case the direct polarization may be subject to some error, but the polar. after inversion be correct, since after the acid treatment the invert sugar shows its normal rotation.

When besides cane and invert sugar a solution contains other optically active substances of a nature not affected in their optical properties by the inversion with hydrochloric acid then Clerget's method is applicable. Casamajor. ‡).

\* Z. V. R. Z, I. 1887, p. 149.

† See Degener (Z. V. R. Z. I. 1886, 347) and Herzfeld loc. cit., 1887, 911.

‡ Chem. News, 45, 150.

If  $D$  = original polarization of the mixture  
 $D_1$  = Rotation after inversion  
 $+R$  the rotation caused by the cane sugar  
 $-J$  the rotation caused by the invert sugar in the orig. solution  
 $+G$  the rotation caused by the foreign dextro-rotatory constituents  
 $-H$  the rotation caused by the foreign lævo-rot. constituents.  
 $-i$  the rotation caused by invert sugar produced from the cane by inversion, we have the expressions

$$\text{Before inversion: } D = +R - J + G - H,$$

$$\text{After " } D_1 = -i - J + G - H$$

and the difference is therefore:

$$D - D_1 = R + i$$

i. e. according to the representations in equation (13):  $a - a_1 = (\varphi_1 c_1) - (\rho k c_1)$ , where in the above case the third member of the equation is negative, on account of lævo-rotation, and therefore enters as positive in the equation.

b By the chemical reaction both substances are changed into new active combination. Representing by

$\varphi_1$  the angular rotation, which 1 g of the substance A dissolved in 100 c. c. exerts in a 1 dm. tube,

$\rho$  the angular rotation which 1 g of the substance A exerts after the inversion.

$\varphi_{11}$  and  $\rho_{11}$  the same angles for the other substance B

$c_1$  and  $c_{11}$  the respective unknown concentrations of the substances A and B, assuming that tubes of the same length were used, the angular rotations of the mixture before inversion  $a$ , and for that after inversion  $a_1$ , are represented by the conditional equations:

$$\begin{aligned} \varphi_1 c_1 + \varphi_{11} c_{11} &= a \\ \rho_1 c_1 + \rho_{11} c_{11} &= a_1, \quad \text{whence} \\ c_1 &= \frac{\rho_{11} a - \varphi_{11} a_1}{\rho_{11} \varphi_1 - \rho_1 \varphi_{11}} \\ c_{11} &= \frac{\rho_1 a - \varphi_1 a_1}{\rho_1 \varphi_{11} - \rho_{11} \varphi_1}. \end{aligned} \quad (14)$$



A case of this kind has been treated by Clerget,\* namely the analysis of a mixture of cane sugar and raffinose. When treated with hydrochloric acid the cane sugar is changed to invert sugar, and the raffinose according to investigations of Hädicke and Tollens into a dextro-rotatory mixture of galactose and laevulose. For the calculations the following figures are used as a basis conditional upon  $l=2$  dm.,  $t=20^\circ$  and the light D:

$\varphi_1 = +1.33^\circ$  angular rot. for 1 g cane sugar, obtained from  $[\alpha]_D = 66.5^\circ$ .

$\rho_1 = -0.425^\circ$  angle resulting from 1 grm. cane sugar after the inversion; calculated for the sp. rotation of invert sugar for a concentration of  $c=15$ , where  $[\alpha]_D = -20.2$ , and 1.0526 g invert sugar = 1 g cane sugar.

$\varphi_{11} = +2.09^\circ$  angular rotation for 1 g raffinose from  $[\alpha]_D = +104.5$ .

$\rho_{11} = +1.06^\circ$  angular rot., for 1 grm. raffinose after inversion, calculated from  $\rho_{11}$ , according to Creydt, that the polarizations of raffinose before and after inversion are in the ratio of 100 : 50.7.

By use of these factors in equation (14) there results for the number of grammes for the two active substances in 100 c. c. the formulas:

$$\text{Cane sugar } c_1 = \frac{1.06a - 2.09a_1}{2.298},$$

$$\text{Raffinose } c_{11} = \frac{0.425a + 1.33a_1}{2.298}.$$

In the investigations of Creydt the inversions were made by heating 50 c. c. of the solution with 5 c. c. of hydrochloric acid of sp. gr. 1.188 for 15 minutes, and after diluting to 100 c. c., observing the deviation in a Ventzke sacchar. at  $20^\circ$ . For converting the degrees into angular degrees the author used for the cane sugar in the original solution the factor 0.3465 and for the inverted solution a medium factor 0.345.

When the Ventzke saccharimeter is used Creydt gives the following formulas for the calculations in which A represents the polarization of the original solution and C the sum of the polar-

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\* L. V. R. Z. I., 1887, 164.

izations before and after the inversion as shown by the saccharimeter :

$$\text{Cane sugar } Z = \frac{C - 0.493 A}{0.827},$$

$$\text{Raffinose } R = \frac{A - Z}{1.57},$$

which give % in 100 parts of the substance in case 26.048 grms. of the latter were dissolved to 100 c. c. dilution.

#### IV.

##### *Use of the Polaristrobometer for the Analysis of Inactive Substances.*

Certain active substances, such as tartaric, malic and asparagic acids, most of the alkaloids, santonin, camphor, etc., show the peculiarity of having their optical activity considerably altered when some inactive substance is added to the solution.

1. For determining the quantity in solution. Preliminary tests are made with solutions of various concentrations of the inactive substance containing always the same quantity of the active substance diluted to the same volume, from the data of which a formula is readily found. As an example the determination of boracic acid in aqueous solution is given. This is accomplished through the aid of tartaric acid whose rotatory power is materially affected by increasing quantities of boracic acid. 20 grms. of tartaric acid were dissolved and diluted to 100 c. c. in solutions of different concentrations of boracic acid and the angular rotation determined with a Laurent half shadow instrument in a 4 dm. tube at 20°. It was found that when  $C$  represented the number of grammes of boracic acid in one litre of solution, and  $a$  the angular rotation of the solution after the addition of the tartaric acid, the relation of the two is expressed by the simple formula

$$C = 1.4a - 14.4.$$

The results as shown from determinations are quite satisfactory, which suggests the use of the method for the rapid determination of boracic acid. It would only be necessary to introduce 20 g. tartaric acid into a 100 c. c. flask, dissolve in the boracic acid solu-

tion, fill up to the mark, and polarize in a 4 dm. tube. By the aid of tartaric acid, or the soluble tartrates, the acids of arsenic and antimony, and also, according to observations of Gernez,\* molybdic and tungstic acids, or their salts, may be determined by means of the angular rotation. Formamide, acetamide and urea, according to Gernez, exert a similar influence as the tartrates. Malic acid is said to be much more sensitive than tartaric acid to the influence of these substances. By the aid of invert sugar the quantity of acetate of lead and possibly other metals could be determined in solutions.

2. Mixtures of two inactive substances may be analyzed by first determining the effect of a number of mixtures of known composition upon the rotatory power of the active substance, using always the same quantity of the latter. The results will be the more favorable the greater the influence of the separate constituents. In this manner possibly the analysis of mixtures of sodium and potassium chloride may be effected.

3. In like manner in certain cases the analysis of a mixture of two inactive solutions may be possible, provided the variations in specific rotation of the added active substance is regular. Thus, according to Oudemans, cinchonine may be used to quantitatively determine small amounts of alcohol in chloroform. Further investigations are needed to determine the usefulness of these methods in special cases.

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\* Compt. rend. 104, 783.

The regular meeting was called for June 7th, 1889.

No quorum.

An informal meeting was held. The secretary announced the receipt of a letter from Kékulé acknowledging the notification of his election to honorary membership.

The following papers were read by Dr. L. H. Friedburg :

1. The reaction of hydrogen peroxide with potassium permanganate, in presence of sulphuric acid. By A. Bourgougnon.

2. Some general considerations on Isomerism (second paper),\*  
by Dr. L. H. Friedburg.

Discussion followed.

DURAND WOODMAN, Rec. Sec'y.

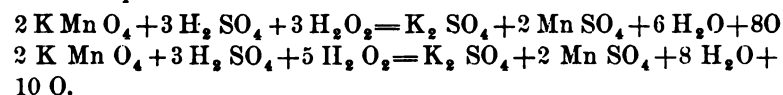
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\* Withdrawn by the author for correction and extension.

ON THE REACTION OF HYDROGEN PEROXIDE WITH  
POTASSIUM PERMANGANATE IN PRESENCE OF  
SULPHURIC ACID.

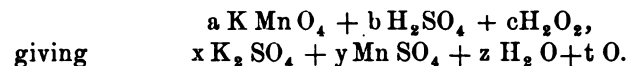
BY A. BOURGOUNNON.

Brodie (Phil. Trans., 1850, 2, 779) investigated the action of hydrogen dioxide upon potassium permanganate in the presence of sulphuric acid, and found that this reaction required three molecules of  $\text{H}_2\text{O}_2$ , whilst other chemists assert that the reaction takes place with five molecules of  $\text{H}_2\text{O}_2$ . In either case, correct equations are obtained.

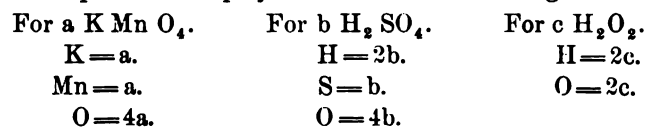


This anomaly can be explained in the following way :

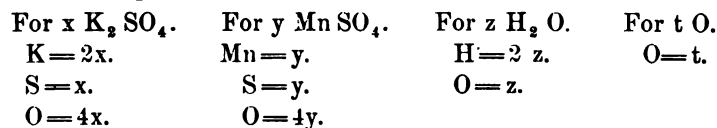
Let us write again the preceding equation without giving any determinate coefficient to the substances employed and obtained in the reaction, in fact, writing this equation in the most indeterminate way.



The products employed for the reaction will give :



And the products of the reaction



Giving the following equations :

$$a = 2x.$$

$$b = x + y.$$

$$4a + 4b + 2c = 4x + 4y + t + z \dots \dots \dots (3)$$

$$a = y$$

$$2b + 2c = 2z,$$

from which

$$x = \frac{a}{2}, y = a, b = x + y = \frac{3a}{2}, z = b + c.$$

Substituting the values of  $b, x, y, z$  in equation (3), gives

$$4a + \frac{12a}{2} + 2c = 2a + 4a + t + b + c,$$

or

$$\frac{8a}{2} + 6a + 2c = 6a + \frac{3a}{2} + t + c.$$

and

$$\frac{8a}{2} - \frac{3a}{2} = t + c - 2c = t - c.$$

$$c = t - \frac{5a}{2}.$$

We have also

$$z = b + c = \frac{3a}{2} + t - \frac{5a}{2} = t - a.$$

Finally we obtain the following values:

$$x = \frac{a}{2}, y = a, b = \frac{3a}{2}, c = t - \frac{5a}{2}, z = t - a.$$

As these results represent whole numbers, it is evident that the smallest value which can be given to  $a$  is 2, because

$$\frac{3a}{2} \text{ and } \frac{5a}{2}$$

represent whole numbers.

Taking  $a = 2$ , the other values become

$$a = 2, x = 1, y = 2, b = 3, c = t - 5, z = t - 2.$$

But  $c$  and  $z$  are whole and positive numbers, then necessarily  $t$  is greater than 5, otherwise  $t - 5$  and  $t - 2$  would be negative. As we must have  $t > 5$ ,  $t$  must be then equal to all the whole numbers, beginning with 6.

Then

$$\begin{aligned} x &= 1. \\ y &= 2. \\ b &= 3. \\ a &= 2. \\ c &= 1, 2, 3, 4, 5, 6 \dots \\ z &= 4, 5, 6, 7, 8, 9, 10 \dots \\ t &= 6, 7, 8, 9, 10, 11 \dots \end{aligned} \left. \vphantom{\begin{aligned} x &= 1. \\ y &= 2. \\ b &= 3. \\ a &= 2. \\ c &= 1, 2, 3, 4, 5, 6 \dots \\ z &= 4, 5, 6, 7, 8, 9, 10 \dots \\ t &= 6, 7, 8, 9, 10, 11 \dots \end{aligned}} \right\} \text{ad infinitum.}$$

If, now, we replace the indeterminate quantities used in the original equation by their values we have



If, keeping  $x=1$ ,  $y=2$ ,  $b=3$ ,  $a=2$ , we take the second values of  $c$ ,  $z$  and  $t$ , we have



and so on, from which we deduce the following simple relation :

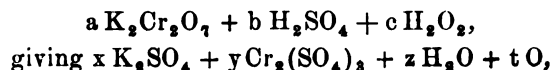
$$\left. \begin{aligned} &\text{Taking } a \text{ of K Mn O}_4 \\ &\text{" } b \text{ of H}_2\text{SO}_4 \\ &\text{and } c \text{ of H}_2\text{O}_2 \end{aligned} \right\} \text{constant.} \\ &\hspace{10em} \text{variable}$$

we obtain a quantity,  $t$ , of free oxygen depending upon the quantity  $c$ , ( $\text{H}_2\text{O}_2$ ) employed, which as in weight  $t$ , oxygen liberated, is equal to  $c$ ; quantity of  $\text{H}_2\text{O}_2$  used in the reaction, *plus 5*.

The study of this reaction shows that this result belongs to the class of indeterminate problems and consequently an infinity of solutions may be obtained, but only in certain positive relations once determined. The quantity  $x$  ( $\text{K}_2\text{SO}_4$ ) and  $y$  ( $\text{Mn SO}_4$ ) are dependent upon  $a$  ( $\text{KMn O}_4$ ) and  $b$  ( $\text{H}_2\text{SO}_4$ ), and for these quantities the amount of  $\text{H}_2\text{O}_2$  to be taken may vary from the minimum,  $c=1$  and for this, corresponding values for  $t$  and  $z$  are obtained.

If potassium dichromate is substituted for potassium permanganate, analogous results are obtained : the final products of the reaction will be potassium sulphate, chromium sulphate, water and oxygen.

We have



from which we obtain

$$\begin{aligned} 2a &= 2x. \\ 2a &= 2y. \\ 7a + 4b + 2c &= 4x + 12y + z + t \dots\dots (3). \\ 2b + 2c &= 2z \dots\dots\dots (4). \\ b &= x + 3y. \end{aligned}$$

giving the following values

$$a = x, x = y, z = b + c, b = 4a, a = \frac{b}{4}$$

Substituting the values of b and y in equation (3) gives

$$7a + 16a + 2c = 4a + 12a + z + t,$$

reducing and subtracting equation (4) we have

$$\begin{aligned} 3a + c &= t. \\ c &= t - 3a. \end{aligned}$$

But t being a whole and positive number we must have

$$t > 3a.$$

Equation (4) gives

$$\begin{aligned} b + c &= 2z. \\ 4a + c &= z \\ c &= z - 4a, \end{aligned}$$

and

$$z > 4a.$$

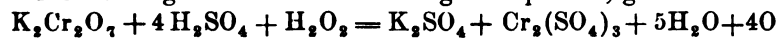
We have then the following values :

$$a = x, x = y, z = b + c, b = 4a, a = \frac{b}{4}$$

Giving to b its smallest value, 4, we find

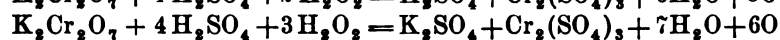
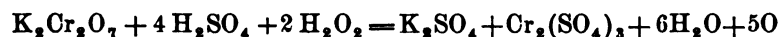
$$\begin{aligned} a &= 1 \\ b &= 4 \\ x &= 1 \\ y &= 1 \\ c &= 1, 2, 3, 4, 5, 6 \dots\dots \\ t &= 4, 5, 6, 7, 8, 9 \dots\dots \\ z &= 5, 6, 7, 8, 9, 10 \dots\dots \end{aligned} \left. \vphantom{\begin{aligned} c \\ t \\ z \end{aligned}} \right\} ad\ infinitum.$$

Introducing these values in the original equation, gives



The other values of c, t and z will give





and so on, from which we deduct the following simple relation :

Taking a of  $\text{K}_2\text{Cr}_2\text{O}_7$  } constant,  
 " b "  $\text{H}_2\text{SO}_4$  }  
 and c "  $\text{H}_2\text{O}_2$  variable,

we obtain a quantity, t, of free oxygen depending upon the quantity c, ( $\text{H}_2\text{O}_2$ ) employed, such as in weight t, oxygen liberated is equal to c, quantity of  $\text{H}_2\text{O}_2$  used in the reaction, *plus 3*.

College of the City of New York, June, 1889.

## NOTE ON LEAD POISONING BY CARBONATED BEVERAGES.

BY DURAND WOODMAN.

In the Summer months of last year (1888) there was an unusual number of cases of lead poisoning in the hospitals of Newark, N. J., the greater part of which were unaccountable, so far as occupation of those suffering was concerned.

In several cases suspicion was strongly directed to bottled beer, soda water and other bottled carbonated beverages, and attention was particularly directed to the patent combination rubber and metal stopper, consisting of a rubber washer held in place by a metal disc.

Qualitative examination proved this disc to be an alloy of lead and tin. Evidences of corrosion were also visible, a gray crust of greater or less depth, according to length of time the stopper had been in use, indicating action of the carbonated liquid on the alloy. Analysis of the alloy gave

Lead .....	46.0
Tin .....	53.2
	<hr/>
	99.2

which corresponds closely with the composition of common solder.

Dr. Herold, of Newark, in a report to the Board of Health, stated that he found two grades of stoppers, one containing lead, 42.4 per cent., practically corresponding to the above analysis, and another containing 83.6 per cent lead, corresponding to common pewter.

In unconcentrated samples of sarsaparilla beer, ginger ale and soda water, when not too highly colored, hydrogen sulphide produced a reaction varying from a mere darkening of the fluid to a distinct precipitate.

The quantities of lead, and in some cases also, of tin, were determined in several samples by evaporating igniting to ash, treating with nitric acid and evaporating, to insure conversion of tin to oxide, then taking up by dilute hydrochloric acid, precipi-

tating by hydrogen sulphide and determining as sulphate in the usual manner.

The quantities found are given in the following tabular statement:

				LEAD.	GRAINS PER GALLON.	
No.		Brand.	Quantity used.	Milligrams found.	Lead.	Tin.
437	Soda Water.	I C V	250 c. c.	3.	0.63	---
438	" "	"	250 c. c.	2.	0.46	1.4
439	Ginger Ale.	C S	-----	---	---	---
440	Soda Water.	O B	675 c. c.	3.7	0.33	---
442	" "	V S M H	1800 c. c.	47.0	1.52	1.63

The last sample, No. 442, was a mixture of several different brands, and the bottles were kept a week lying on their sides before opening them.

It will be observed that more tin has been dissolved than lead. Proust is authority for the statement that from an alloy of lead 75, tin 25, vinegar dissolves tin only. (Watts III., 535.) A small amount of copper, not determined, was also found in No. 442, probably from some vessel or pipe at the bottling establishments.

In considering these figures, it is to be taken into account that ordinary bottled soda water is flavored with lemon, perhaps reinforced by citric acid, which would be another factor in the solvent action due to the carbonated liquid.

In experiments made with carbonated water alone, Dr. Herold reported finding 0.52 grain of lead per gallon after only two days' contact with the stoppers, under the same conditions of pressure.

Of a number of samples recently examined from bottles closed by ordinary corks, several have responded slightly to hydrogen sulphide, indicating, as above mentioned, that a part of the dissolved metals has its source in the vessels and transfer pipes at the bottling establishment.

The general result of the attention called to the subject has been, however, a marked improvement, due to the substitution of ordinary corks and rubber stoppers by the leading manufacturers.

## THE CHEMICAL PROBLEMS OF TO-DAY.

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An address delivered at Heidelberg at the first general session of the sixty-second meeting of The Association of German Naturalists and Physicians, Sept. 18, 1889,\*

BY VICTOR MEYER,

TRANSLATED BY L. H. FRIEDBURG.

When, a short time ago, I was called upon to speak before you, I gladly and zealously approached the work, which such an occasion seemed to call forth. It seemed to me that it would be an effort worthy of this assemblage of scientific men to recall the permanent additions that chemistry has made in our day to the treasure of human knowledge and to enumerate the problems which seem to lie nearest us in the future.

A science which, as such, is hardly older than the great European revolution, the centennial of which we witnessed a few months ago, and which in this short time has caused changes in our spiritual and material life hardly less than those of the political revolution, such a science, I have thought, may, without temerity boast of its achievements.

And yet the chemist approaches such a task, with a certain hesitation, from which the astronomer, the physicist and the mathematician are free. Has it not been in our own day that the most prominent orator amongst German naturalists, one who astonishes us by the comprehensiveness of his knowledge, has adopted as his own Kant's judgment on chemistry, namely that "chemistry is a science, but not a science in the highest sense of the word, that is, a knowledge of nature reduced to mathematical mechanics." And this dictum is accepted, not

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\*Deutsche Rundschau. Nov., 1889.

as a blemish upon our science, but with the fullest and most perfect recognition of the immense achievements which modern chemistry has registered as its own.

But all of the marvelous successes of the atomic theory and of the doctrine of structure; the synthesis of the most complicated organic compounds; the blessings of an enlarged pharmacopia, the potent revolution in technological processes, the new and systematic methods of production which have been characterized by an eminent technologist as "the gaining of gold from rubbish"—all this seems trifling to the mind that looks down from its standpoint of mathematical mechanics when compared with the work of a promised Newton of chemistry, who some day will represent chemical reactions in the thought and in the language of mathematical physics.

And if he who looks from a height is justified in the expression that to-day chemistry, in the recognition of ultimate causes, stands yet below astronomy of the time of Kepler and Copernicus, must not the chemist lose courage if he attempts, before an illustrious assemblage, to raise a song of praise to his science, to glorify what she has done and what in the future she seems chosen to do? If in spite of this the attempt be made, it must be with that resignation which rests upon the belief that "we should consider everything but to aim only at that which is possible."

Though we share, with full conviction, the expectations of a Newtonian period in chemistry, we hardly venture to hope that that period is near, and even the most enlightened representatives of the newer physical chemistry seem but precursors of that distant era.

Perhaps the chemist, immersed in the daily work of his science, fails to take the comprehensive view of one who from a distant height looks down upon the same. But those who are surrounded by the whirl of hourly renewed work recognize, all the more clearly, the immense amount that remains still to be achieved before those distant aims can be realized. This epoch, so rich in path finders in the department of physics, has rarely directed the highest order of research into the territory of our science and especially have the more complicated chemical phenomena been avoided.

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success in this direction is only granted to the genius—the method that leads onward cannot be learned, and it has only been practiced with success by a small number of chosen ones.

Indeed, in the experimental study of organic chemistry, the “presentiment” of happenings, the actuality of which is not indicated by any law to be expressed in words, has shown surprising results: here the thought is aided by a something, which we may meanwhile term “chemical feeling,” a name which will disappear as soon as the progressive approach of chemistry to the mathematical physical basis shall have disclosed its meaning and shall have tabulated it amongst the methods which lead to the recognition of the new. The effect of this peculiar chemical method of study is not here to be dwelt upon in detail. Let it suffice to say, that without it the most brilliant discoveries in organic chemistry would not have been made, just as little as a Kekulé would, without it, have been unable, in contradiction of numerous data in chemical literature never before doubted, to affirm the non-existence of isomeric monochlorbenzol and of such bodies as were said to consist of a benzol ring and but *one* bivalent atom. Those significant hypotheses by means of which the knowledge of aromatic substances has been revealed to us, could not have been made solely upon the ground of exact observation, they required at the same time a pronounced chemical instinct. There was no logical reason in declaring the existence of a phenylene oxide as an impossibility, since the ethylene oxide did exist; he who nevertheless ventured to do so and at the same time ran directly in the face of experience, was surely led by a feeling which the present status of chemistry forbids us to replace by a process of thought.

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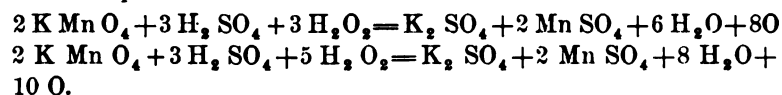
If now we begin to consider—within the appointed limits—the most important achievements of chemistry, we cannot, at this place and at this hour of our meeting, be in doubt as to what is to be mentioned in the first place. The hospitable city that shelters us boasts of an advantage which is envied her by every other *Alma Mater*: here, chemistry for more than a human lifetime has been represented by Robert Bunsen, of glorious name, and the very days which find us here assembled, follow immediately the moment in which this hero of science has retired from his academical occupation. Who does not think, at such an hour, of the great teacher around whom ardent pupils from all parts of the globe were accustomed to congregate. But who, being called upon to-day to speak of the results of chemistry within the walls of Heidelberg, would not before all direct an eye upon that one discovery which has lifted chemistry beyond terrestrial research, which has enabled her, like astronomy, to search the universe and to dissect the starry heavens, chemically, by the subtle appliances of analysis. If “old Heidelberg” has become a pearl amongst German cities by its history, by its numerous traditions, by the incomparable beauty of its situation—if its university is the ideal of the German academical youth, we may well regard as an immortal leaf in its wreath of honor, along with these glorious titles, the union of those two great men who first met in this city in the most courageous enterprise of the penetrating mind; who have pursued with astonishing success the investigation which has made spectral analysis the most potent of scientific weapons, and has rendered their names a charm calling forth the admiration of the older minds and kindling in the minds of mere school-boys the flame of enthusiasm in the study and exploration of



ON THE REACTION OF HYDROGEN PEROXIDE WITH  
POTASSIUM PERMANGANATE IN PRESENCE OF  
SULPHURIC ACID.

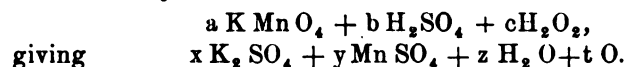
By A. BOURGOUENON.

Brodie (Phil. Trans., 1850, 2, 779) investigated the action of hydrogen dioxide upon potassium permanganate in the presence of sulphuric acid, and found that this reaction required three molecules of  $\text{H}_2\text{O}_2$ , whilst other chemists assert that the reaction takes place with five molecules of  $\text{H}_2\text{O}_2$ . In either case, correct equations are obtained.

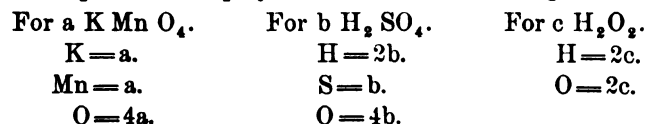


This anomaly can be explained in the following way :

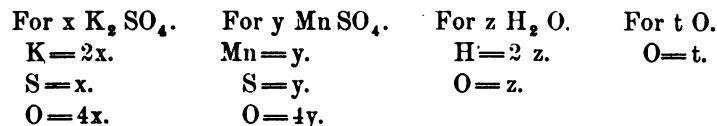
Let us write again the preceding equation without giving any determinate coefficient to the substances employed and obtained in the reaction, in fact, writing this equation in the most indeterminate way.



The products employed for the reaction will give :



And the products of the reaction



Giving the following equations :

$$\begin{aligned} a &= 2x. \\ b &= x+y. \\ 4a + 4b + 2c &= 4x + 4y + t + z \dots\dots\dots (3) \\ a &= y \\ 2b + 2c &= 2z, \end{aligned}$$

from which

$$x = \frac{a}{2}, y = a, b = x + y = \frac{3a}{2}, z = b + c.$$

Substituting the values of b, x, y, z in equation (3), gives

$$4a + \frac{12a}{2} + 2c = 2a + 4a + t + b + c,$$

or

$$\frac{8a}{2} + 6a + 2c = 6a + \frac{3a}{2} + t + c.$$

and

$$\frac{8a}{2} - \frac{3a}{2} = t + c - 2c = t - c.$$

$$c = t - \frac{5a}{2}.$$

We have also

$$z = b + c = \frac{3a}{2} + t - \frac{5a}{2} = t - a.$$

Finally we obtain the following values:

$$x = \frac{a}{2}, y = a, b = \frac{3a}{2}, c = t - \frac{5a}{2}, z = t - a.$$

As these results represent whole numbers, it is evident that the smallest value which can be given to a is 2, because

$$\frac{3a}{2} \text{ and } \frac{5a}{2}$$

represent whole numbers.

Taking  $a = 2$ , the other values become

$$a = 2, x = 1, y = 2, b = 3, c = t - 5, z = t - 2.$$

But c and z are whole and positive numbers, then necessarily t is greater than 5, otherwise  $t - 5$  and  $t - 2$  would be negative. As we must have  $t > 5$ , t must be then equal to all the whole numbers, beginning with 6.

Then

$$\begin{aligned} x &= 1. \\ y &= 2. \\ b &= 3. \\ a &= 2. \\ c &= 1, 2, 3, 4, 5, 6 \dots \\ z &= 4, 5, 6, 7, 8, 9, 10 \dots \\ t &= 6, 7, 8, 9, 10, 11 \dots \end{aligned} \left. \vphantom{\begin{aligned} x &= 1. \\ y &= 2. \\ b &= 3. \\ a &= 2. \\ c &= 1, 2, 3, 4, 5, 6 \dots \\ z &= 4, 5, 6, 7, 8, 9, 10 \dots \\ t &= 6, 7, 8, 9, 10, 11 \dots \end{aligned}} \right\} ad\ infinitum.$$

If, now, we replace the indeterminate quantities used in the original equation by their values we have



If, keeping  $x=1$ ,  $y=2$ ,  $b=3$ ,  $a=2$ , we take the second values of  $c$ ,  $z$  and  $t$ , we have



and so on, from which we deduce the following simple relation :

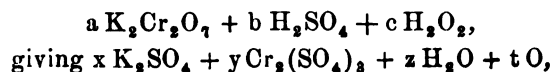
$$\begin{aligned} &\text{Taking } a \text{ of K Mn O}_4 \left. \vphantom{\begin{aligned} &\text{Taking } a \text{ of K Mn O}_4 \\ &\text{b of H}_2\text{SO}_4 \\ &\text{and } c \text{ of H}_2\text{O}_2 \end{aligned}} \right\} \text{constant.} \\ &\text{b of H}_2\text{SO}_4 \\ &\text{and } c \text{ of H}_2\text{O}_2 \quad \text{variable} \end{aligned}$$

we obtain a quantity,  $t$ , of free oxygen depending upon the quantity  $c$ , ( $\text{H}_2\text{O}_2$ ) employed, which as in weight  $t$ , oxygen liberated, is equal to  $c$  ; quantity of  $\text{H}_2\text{O}_2$  used in the reaction, *plus 5*.

The study of this reaction shows that this result belongs to the class of indeterminate problems and consequently an infinity of solutions may be obtained, but only in certain positive relations once determined. The quantity  $x$  ( $\text{K}_2\text{SO}_4$ ) and  $y$  ( $\text{Mn SO}_4$ ) are dependent upon  $a$  ( $\text{KMn O}_4$ ) and  $b$  ( $\text{H}_2\text{SO}_4$ ), and for these quantities the amount of  $\text{H}_2\text{O}_2$  to be taken may vary from the minimum,  $c=1$  and for this, corresponding values for  $t$  and  $z$  are obtained.

If potassium dichromate is substituted for potassium permanganate, analogous results are obtained : the final products of the reaction will be potassium sulphate, chromium sulphate, water and oxygen.

We have



from which we obtain

$$\begin{aligned} 2a &= 2x. \\ 2a &= 2y. \\ 7a + 4b + 2c &= 4x + 12y + z + t \dots\dots (3). \\ 2b + 2c &= 2z \dots\dots\dots (4). \\ b &= x + 3y. \end{aligned}$$

giving the following values

$$a = x, x = y, z = b + c, b = 4a, a = \frac{b}{4}$$

Substituting the values of b and y in equation (3) gives

$$7a + 16a + 2c = 4a + 12a + z + t,$$

reducing and subtracting equation (4) we have

$$\begin{aligned} 3a + c &= t. \\ c &= t - 3a. \end{aligned}$$

But t being a whole and positive number we must have

$$t > 3a.$$

Equation (4) gives

$$\begin{aligned} b + c &= 2z. \\ 4a + c &= z \\ c &= z - 4a, \end{aligned}$$

and

$$z > 4a.$$

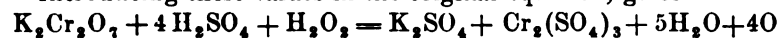
We have then the following values :

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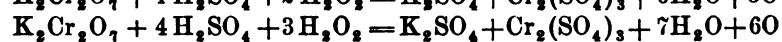
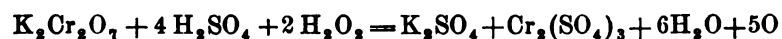
Giving to b its smallest value, 4, we find

$$\begin{aligned} a &= 1 \\ b &= 4 \\ x &= 1 \\ y &= 1 \\ c &= 1, 2, 3, 4, 5, 6 \dots\dots \\ t &= 4, 5, 6, 7, 8, 9 \dots\dots \\ z &= 5, 6, 7, 8, 9, 10 \dots\dots \end{aligned} \left. \vphantom{\begin{aligned} a &= 1 \\ b &= 4 \\ x &= 1 \\ y &= 1 \\ c &= 1, 2, 3, 4, 5, 6 \dots\dots \\ t &= 4, 5, 6, 7, 8, 9 \dots\dots \\ z &= 5, 6, 7, 8, 9, 10 \dots\dots \end{aligned}} \right\} ad infinitum.$$

Introducing these values in the original equation, gives



The other values of c, t and z will give



and so on, from which we deduct the following simple relation :

Taking a of  $\text{K}_2\text{Cr}_2\text{O}_7$  } constant,  
 " b "  $\text{H}_2\text{SO}_4$  }  
 and c "  $\text{H}_2\text{O}_2$  variable,

we obtain a quantity, t, of free oxygen depending upon the quantity c, ( $\text{H}_2\text{O}_2$ ) employed, such as in weight t, oxygen liberated is equal to c, quantity of  $\text{H}_2\text{O}_2$  used in the reaction, *plus 3*.

College of the City of New York, June, 1889.

## NOTE ON LEAD POISONING BY CARBONATED BEVERAGES.

BY DURAND WOODMAN.

In the Summer months of last year (1888) there was an unusual number of cases of lead poisoning in the hospitals of Newark, N. J., the greater part of which were unaccountable, so far as occupation of those suffering was concerned.

In several cases suspicion was strongly directed to bottled beer, soda water and other bottled carbonated beverages, and attention was particularly directed to the patent combination rubber and metal stopper, consisting of a rubber washer held in place by a metal disc.

Qualitative examination proved this disc to be an alloy of lead and tin. Evidences of corrosion were also visible, a gray crust of greater or less depth, according to length of time the stopper had been in use, indicating action of the carbonated liquid on the alloy. Analysis of the alloy gave

Lead .....	46.0
Tin .....	53.2
	<hr/>
	99.2

which corresponds closely with the composition of common solder.

Dr. Herold, of Newark, in a report to the Board of Health, stated that he found two grades of stoppers, one containing lead, 42.4 per cent., practically corresponding to the above analysis, and another containing 83.6 per cent lead, corresponding to common pewter.

In unconcentrated samples of sarsaparilla beer, ginger ale and soda water, when not too highly colored, hydrogen sulphide produced a reaction varying from a mere darkening of the fluid to a distinct precipitate.

The quantities of lead, and in some cases also, of tin, were determined in several samples by evaporating igniting to ash, treating with nitric acid and evaporating, to insure conversion of tin to oxide, then taking up by dilute hydrochloric acid, precipi-

tating by hydrogen sulphide and determining as sulphate in the usual manner.

The quantities found are given in the following tabular statement:

No.		Brand.	Quantity used.	LEAD.	GRAINS PER GALLON.	
				Milligrams found.	Lead.	Tin.
437	Soda Water.	I C V	250 c. c.	3.	0.63	---
438	" "	"	250 c. c.	2.	0.46	1.4
439	Ginger Ale.	C S	-----	--	---	---
440	Soda Water.	O B	675 c. c.	3.7	0.33	---
442	" "	V S M H	1800 c. c.	47.0	1.52	1.63

The last sample, No. 442, was a mixture of several different brands, and the bottles were kept a week lying on their sides before opening them.

It will be observed that more tin has been dissolved than lead. Proust is authority for the statement that from an alloy of lead 75, tin 25, vinegar dissolves tin only. (Watts III., 535.) A small amount of copper, not determined, was also found in No. 442, probably from some vessel or pipe at the bottling establishments.

In considering these figures, it is to be taken into account that ordinary bottled soda water is flavored with lemon, perhaps reinforced by citric acid, which would be another factor in the solvent action due to the carbonated liquid.

In experiments made with carbonated water alone, Dr. Herold reported finding 0.52 grain of lead per gallon after only two days' contact with the stoppers, under the same conditions of pressure.

Of a number of samples recently examined from bottles closed by ordinary corks, several have responded slightly to hydrogen sulphide, indicating, as above mentioned, that a part of the dissolved metals has its source in the vessels and transfer pipes at the bottling establishment.

The general result of the attention called to the subject has been, however, a marked improvement, due to the substitution of ordinary corks and rubber stoppers by the leading manufacturers.

## THE CHEMICAL PROBLEMS OF TO-DAY.

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An address delivered at Heidelberg at the first general session of the sixty-second meeting of The Association of German Naturalists and Physicians, Sept. 18, 1889,\*

BY VICTOR MEYER,

TRANSLATED BY L. H. FRIEDBURG.

When, a short time ago, I was called upon to speak before you, I gladly and zealously approached the work, which such an occasion seemed to call forth. It seemed to me that it would be an effort worthy of this assemblage of scientific men to recall the permanent additions that chemistry has made in our day to the treasure of human knowledge and to enumerate the problems which seem to lie nearest us in the future.

A science which, as such, is hardly older than the great European revolution, the centennial of which we witnessed a few months ago, and which in this short time has caused changes in our spiritual and material life hardly less than those of the political revolution, such a science, I have thought, may, without temerity boast of its achievements.

And yet the chemist approaches such a task, with a certain hesitation, from which the astronomer, the physicist and the mathematician are free. Has it not been in our own day that the most prominent orator amongst German naturalists, one who astonishes us by the comprehensiveness of his knowledge, has adopted as his own Kant's judgment on chemistry, namely that "chemistry is a science, but not a science in the highest sense of the word, that is, a knowledge of nature reduced to mathematical mechanics." And this dictum is accepted, not

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\*Deutsche Rundschau. Nov., 1889.



as a blemish upon our science, but with the fullest and most perfect recognition of the immense achievements which modern chemistry has registered as its own.

But all of the marvelous successes of the atomic theory and of the doctrine of structure; the synthesis of the most complicated organic compounds; the blessings of an enlarged pharmacopia, the potent revolution in technological processes, the new and systematic methods of production which have been characterized by an eminent technologist as "the gaining of gold from rubbish"—all this seems trifling to the mind that looks down from its standpoint of mathematical mechanics when compared with the work of a promised Newton of chemistry, who some day will represent chemical reactions in the thought and in the language of mathematical physics.

And if he who looks from a height is justified in the expression that to-day chemistry, in the recognition of ultimate causes, stands yet below astronomy of the time of Kepler and Copernicus, must not the chemist lose courage if he attempts, before an illustrious assemblage, to raise a song of praise to his science, to glorify what she has done and what in the future she seems chosen to do? If in spite of this the attempt be made, it must be with that resignation which rests upon the belief that "we should consider everything but to aim only at that which is possible."

Though we share, with full conviction, the expectations of a Newtonian period in chemistry, we hardly venture to hope that that period is near, and even the most enlightened representatives of the newer physical chemistry seem but precursors of that distant era.

Perhaps the chemist, immersed in the daily work of his science, fails to take the comprehensive view of one who from a distant height looks down upon the same. But those who are surrounded by the whirl of hourly renewed work recognize, all the more clearly, the immense amount that remains still to be achieved before those distant aims can be realized. This epoch, so rich in path finders in the department of physics, has rarely directed the highest order of research into the territory of our science and especially have the more complicated chemical phenomena been avoided.

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nature. The immeasurable results of that discovery—the consequences of which extend every day over new territories—are known in the widest circles and to mention them to-day in detail would be but carrying owls to Athens. It behooves us in this place to mention reverently the names of B u n s e n and K i r c h h o f f, to think of them with gratitude, and to hope that men, their equals, may not be entirely wanting in the next generation! The younger one of them—whose scientific fertility was only equaled by his greatness of soul and the charming modesty of his heart—has been taken away from us before old age had naturally limited him. B u n s e n we still rejoice to call ours, who now, allowing the tools of his work to drop from his hand, looks forth to the evening of his life in quiet, happy leisure. May he be permitted for a long time to look back upon a life filled with greatest scientific achievements; may his calm, friendly eye rest for many years upon the incomparable picture of his beloved Heidelberg.

We have mentioned spectral analysis, though it has been almost for an age the common property of science. Let us also cast a grateful retrospect upon a deeply furrowing revolution—of which chemistry also, for several decades, has boasted as a substantial possession—upon the development of the *doctrine of structure*, that solid theoretical foundation from which the proud edifice of modern organic chemistry rises. A generation has grown up around us which has received as a matter of fact this doctrine which still seems new to us older ones. But those far-seeing men, whose eyes recognized the immensely simple in the seemingly impenetrable complication of the carbon compounds, are still actively alive amongst us, and it is their happy lot to reap in their own activity what once they sowed in juvenile work. Here the eye is directed upon the master of chemical research—A u g u s t W i l h e l m v o n H o f m a n n; before all upon his researches upon the organic nitrogenous bases—researches which do not find their equal in organic chemistry and which, even more perfectly than D u m a s' fundamental discovery of trichloroacetic acid, allowed the fundamental conception of substitution to expand into the living consciousness of chemists, at first, curiously, by supporting the theory of types in organic compounds and then

by promoting the transition to the structural or constitutional view, which at present embraces, with unparalleled perfection, the whole territory of organic compounds.

But the suggestion of this doctrine, which finds its crowning success in the recognition of the inner aggregation of the atoms, is associated for all time with the name of a man who, although a master of rare art in experimenting, knew how to surpass what he had achieved at the laboratory table by the convincing power of his speculative work. We cannot here dispute the part which other eminent chemists have taken in the development of the doctrine of structure—there are, Butlerow, Cooper, Erlenmeyer, Frankland, Kolbe, Odling, Williamson—but the glorious guide in this great and victorious movement forward, he, to whose eyes was disclosed not only the tetravalence of carbon, but also the solution of the problem of the constitution of organic compounds, in the recognition of the property of carbon atoms to be linked to *each other* by their valencies; he is the *philosopher* of organic chemistry—August Kekulé. The name of this discoverer, who also started upon his high and soaring flight from Heidelberg, is justly mentioned *alone* when we want to recall in a word the putting forth and the development of the leading chemical theories.

The researches in this direction are so numerous and so toilsome, and yet the result is so surprisingly simple! The carbon atom is endowed with four, the oxygen atom with two, the hydrogen atom with one point of attack for the chemical affinity. The cause of the aggregation of the atoms within the molecule lies in the mutual saturation of these units of affinity or valencies. It is the number of valencies which decides the possibility of the existence of a compound. Amongst the legion of imaginable combinations of these three elements only those are capable of existence in which every valency is saturated by that of another atom. Through this knowledge a new method of inquiry was opened, in particular for organic chemistry, the immense territory of which for many years seemed totally to absorb the working power of chemists. But then dawned the first signs of a further development, Hardly a decade had elapsed since the general admission

of the doctrine of valency, when a fundamental deepening of the same was announced, which our science owes to two savants, working independently of each other—to Le Bel and van't Hoff. These chemists, considering those substances which turn the plane of polarization of light, arrived at views which soon led to a result, until then thought to be out of reach, a conception of the aggregation of the atoms within the molecules in space. Thus a field of study was created which van't Hoff called "*la chimie dans l'espace*" and which we now call *Stereo-chemistry*.

It was recognized that the carbon atom stretched out its four valencies in definite directions, and this in a symmetrical manner. The combination of a carbon atom with four other atoms, for example methane,  $\text{CH}_4$ , is representable by the picture of a tetrahedron in the stereometric centre of which the carbon atom is situated, while the hydrogen atoms occupy its four corners.

Numerous cases of isomerism until then not understood, could be explained in this manner and were regarded as stereochemical ones. The cause of optical activity was found to consist in the presence of an asymmetric carbon atom, that is, one which is combined with four different groups.

Also the stereometric forms of a few simple molecules were considered; it was recognized, e. g. that a compound of three carbon atoms linked together by one bond respectively, could not contain those atoms in a straight line, but that they must lie in the angles of a triangle the sides of which form an angle equal to that in which the directions of valency of the carbon atom intersect each other.

By the application of these considerations to more complicated molecules, which contain a chain of atoms closed within itself, Adolph von Baeyer has enlarged our theory in a manner full of consequence.

Kekulé in times past had recognized that carbon shows a particular disposition to form *closed* chains of six atoms. The discoveries of Baeyer and his followers as well as Fittig's work on lactones, taught that such closed chains or rings formed of fewer atoms also exist. But while rings of six or five atoms easily form, it is more difficult to combine fewer atoms, four or

three, to a closed chain. The cause of this fact Baeyer recognized as lying in the stereometric conditions. The angles which the sides of a regular hexagon and pentagon form with each other very nearly coincide with those, in which the directions of the valencies of the carbon atom intersect each other, and thus, in linking five or six atoms together, the circle, so to speak, closes itself, while if more or less atoms are present this can only be arrived at by strong deviation of the directions of affinity.

But still more surprising discoveries were hidden in van't Hoff's theory. The gifted Dutch thinker had penetrated to the idea that two atoms which are linked together by a single valency rotate freely around an axis the direction of which coincides with that of the linking valency, but that this rotation is stopped as soon as double linking takes place. This latter is an immediate consequence of the tetrahedric conception. If I stretch out my forefingers and let their points touch each other, then the hands can rotate around them as an axis; but if I stretch both thumbs and both forefingers and allow their corresponding points to touch each other, then a system results in which rotation is impossible.

These two propositions of van't Hoff having remained almost unnoticed for a decade, have lately come into great prominence. In a series of important researches Johannes Wislicenus has proved, that, applying these propositions and at the same time considering the specific affinities of the groups or elements present, the stereometric aggregation of the atoms in certain molecules can be determined with probability. In an ingenious manner he has utilized the addition phenomena shown by carbon atoms trebly linked together for an interpretation of a stereometric aggregation of the atoms in the compounds formed.

Wislicenus, applying van't Hoff's ideas with courage and strictness, has advanced organic chemistry in an important manner and has opened a field for experimental research, which heretofore had been avoided with a precaution suggestive of timidity.

New discoveries came from other sides. An intimate research into the oxims of benzil lead to the surprising result, that the validity of the second proposition of van't Hoff is not with-



out exception. Cases were noticed, in which the free rotation of carbon atoms united by a *simple* bond, which v a n ' t H o f f disclosed, did not obtain. Further inquiry into this subject led to a renewal of the question, "What does *chemical valency* really mean?" A question to which the mind incessantly demands an answer. It had long since been suggested that valency had some relation to the electric behavior of the atoms. The chemistry of the day expresses F a r a d a y ' s fundamental electrolytic law thus: an electric current which flows through several fused electrolytes, severs in each of them the same number of *valencies*—not of *atoms*.

It was found by v o n H e l m h o l t z that those quantities of electricity which, during the electrolytic process, move with the ions, are distributed among the valencies. R i e c k e, in virtue of his pyroelectric researches, was led to the view that the atoms are surrounded by certain systems of positive and negative electric poles.

Uniting these results with those of purely chemical experimentation, we arrive at the idea that the valencies do not appear as *points* of attack proper, but as having *linear* dimensions. The carbon atom represents itself as a sphere, surrounded by an envelope of ether which contains the valencies. The latter seem to be determined by the presence of two opposite electric poles which rest at the ends of a very short straight line. Such a system is called a *dipole*. The attachment of two valencies to each other consists in the attraction of their opposed poles. It is evident that in a radial position of the dipoles, they form an axis around which the atoms are able to rotate, but that this rotation is upset in case of a tangential position. In what has been said so far and through further considerations in regard to the electrical charge of the atoms and of the dipoles, a reason is found for the repulsion of the four valencies and consequently for the tetraedric grouping of the same.

The fact that the valencies can deviate from this position now becomes intelligible; we perceive why the valencies of *one* atom cannot unite with one another, while those of different atoms can combine; it is clear that there can exist two kinds of simple link-

ing, one of which admits of rotation, while the other does not; finally that in cases of manifold linking the free rotation must be annulled. Hence this hypothesis opens to us an understanding of the most important properties of chemical valency.

So much may be said of the problems relating to the theory of valency.

But the doctrine of substitution has likewise experienced a peculiar enlargement. D u m a s first showed that the properties of organic compounds are generally little changed when the hydrogen of the same is replaced by univalent elements or groups. Now it has been learned from later experiments that even much more radical changes in the composition do not materially influence the properties of the substance. If, for example, we replace in the hydrocarbon *benzol* two carbon and two hydrogen atoms by one atom of sulphur, the resulting product, *thiophen*, resembles *benzol*, chemically and physically, so closely as to be mistaken for it. We learn from this that the sulphur atom is able to take upon itself the functions of four atoms of entirely different nature. Similar facts have been found in regard to oxygen and to the imido group, which is equivalent to it.

Turning away from these researches to cast a glance upon general chemical studies which lie some years behind us, we must above all consider one of the most far reaching discoveries of our epoch, the revelation of the *natural system of the chemical elements*. We owe this to the far seeing D e m e t r i u s M e n d e l e j e f f. By the side of the titanic figure of the Russian scholar we see the Englishman, N e w l a n d s, and our own countryman, L o t h a r M e y e r, successfully co-operating in the foundation and the structure of this work. What these men created has since become generally known: *they showed that the properties of the elements are functions of their atomic weights*. M e n d e l e j e f f taught us to predict the existence and the properties of chemical elements as yet unknown, with a certainty that reminds us of L e V e r r i e r's prediction of the discovery of the planet Neptune. We can say with accuracy that even to-day numerous elements, the qualities of which, as well as the place which they will occupy in the system, can be minutely foretold, wait merely to be discovered.

The natural system has imposed upon us a problem of the greatest significance in the new determination of the atomic weights, the numerical values of which are now of increased interest. But numerous other problems are presented by the new system of the elements. Above all we are at a loss to discern the cause of the inner nexus of the elements as the system offers it. Also by diligent work the less studied elements must be properly brought within the system. Fortunate circumstances may allow us to discover the numerous elements indicated by the periodic law. Here let us note a peculiar coincidence. We know to-day about seventy elements, but Mendeleeff's table indicates so far two small periods of seven elements each and five large ones of seventeen elements respectively. To these must be added hydrogen forming a "group" in itself.

By addition of these figures,  $2 \times 7 + 5 \times 17 + 1$ , we obtain exactly the number 100.

It is true that no one can say whether the missing elements will really be discovered or if further new periods might not be indicated by which this number 100 would be exceeded. But, as far as positive data are at hand, they indicate exactly the number mentioned and nothing points beyond it. An odd coincidence which seems to ally the number of the existing elements with the number of our fingers.

The discovery of the system of the elements leads us back to the question whether the chemical elements are separate worlds in themselves or whether they represent different forms or conditions under which *one* ultimate substance exists; a question that has occupied the philosophical mind since very early times. The same question was raised anew by the discovery of spectral analysis. Whosoever regards the numerous lines of the spectrum of a metal will hardly be convinced that the metal from which they emanate should be an eternally indecomposable element. In a similar manner the compound nature of the elements is indicated by comparison of the regularities in numbers of the atomic weights with the homologous series of organic chemistry.

In the pursuit of this question, which, since *Prout's* hypothesis and the surprises offered by *Stas's* determinations of atomic

weights, has not been allowed to rest, positive results are not to be found. The decomposition of substances called elements into simpler ones has not been accomplished.

Nevertheless something has been achieved, since an increased interest has been drawn towards pyro-chemical research.

To-day, new methods of experiment permit of a comparatively easy determination of the vapor density, and consequently of the molecular state of the substances at the highest temperatures.

Numerous inorganic compounds, above all the very elements, have been studied in regard to their vapor density at a white heat.

While many of them, as oxygen, nitrogen, sulphur and mercury remain unchanged under such conditions, the molecules of chlorine, bromine and iodine respectively, were split into two atoms, in conformity with Avogadro's surmise of the compound nature of elementary molecules.

In the same manner, the vapor density and the molecular condition of the less volatile substances, zinc, thallium, antimony and bismuth, was successfully determined at a white heat.

Careful research resulted in the exposure of the old fallacy of the existence of a sulphur molecule containing six atoms.

But how many of the problems which crowd around us at this point are for the time being entirely beyond the reach of the experimenter !

To-day, pyrochemical work is limited to a temperature of 1700° C, because vessels of porcelain and platinum, to the use of which we are limited, fuse above that temperature. The possibility of performing quantitative experiments at these temperatures seemed to us some years ago to be an unexpected progress, but to-day we complain that the trivial cause of a want of proper vessels forbids us to increase the temperature up to 2000° or 3000° C. There is no doubt that we should arrive at new unthought of facts, that the splitting of still other elementary molecules would be possible, that a new chemistry would be revealed to us if, being provided with vessels of infusible material, we could work at temperatures at which water could not exist and at which detonating gas would be a non-inflammable mixture !

Let us now enter other fields of physical chemistry. Golden

fruit, daily increasing, has been harvested upon this field during these latter days. Again we see van't Hoff take the lead. His keen eye has enabled us to penetrate the nature of *solution*, which forms the beginning of a new epoch in molecular physics. The quintessence of his discoveries may be thus expressed :

“Solutions of different substances in the same liquid, which contain in the same volume *an equal number of molecules* of the dissolved substance, show the same *osmotic pressure, the same vapor pressure, and the same freezing point.*”

This surprising generalization offers the possibility of determining *the true molecular weight of substances* by experimenting upon them in *solution*, while heretofore this has only been possible by transforming them into the gaseous state, hence only for volatile substances, since *dilute solutions* behave in regard to the molecular state of the dissolved substance like *gases*.

In this manner new methods are given for the determination of molecular weights, which we are now able to determine by means of measurements relating to the *freezing point*, the *vapor pressure* or the *osmotic pressure* of a solution of the substance to be tested.

These results are of the highest possible practical importance for chemistry, since they widen in an unexpected manner the possibility of the determination of molecular weights, and in a still higher degree we are surprised by the elucidation which they offer in regard to *the nature of solution*. Clausius had already admitted within narrower limits, that in solutions of electrolytes, some of the dissolved molecules were decomposed into their ions, but now this has been proved in a larger measure, particularly by Arrhenius. What a change our conceptions will have to undergo if we have to accustom ourselves to regard a dilute solution of sodium chloride as one containing, not undecomposed molecules of this salt, but separated atoms of sodium and chlorine !

We owe these revolutionizing innovations to the investigations of van't Hoff, Arrhenius, Ostwald, Planck and de Vrie but, in regard to experimental research, especially to the splendid work of Raoult, which during recent years has effected this mighty theoretical progress.

Thus we see Physical Chemistry moving on in weighty development. Special laboratories are opened for her and a special journal also has been started which is open alike to the records of experiment and to theoretical discussion. Through the foundation of this organ physical chemistry has been furthered in a most active manner. All the questions of the time and all those in dispute belonging to this department of science receive in this paper a thorough discussion. Dynamical-chemical questions are successfully studied, a significant impetus is given to the study of structure and affinity, (widened as our knowledge of the nature of solutions has made necessary) by means of the study of the relations between chemical nature and electric conduction.

The inquiry into the intimate relations that exist between physical and chemical properties, which was inaugurated half a century ago by Hermann Kopp, is now being deepened and widened.

It is true that the great hopes which sprang from the study of thermo-chemical questions have so far been only partly fulfilled, but consecutive measurements offer more clearness also in this case.

There is no field of our science in which we may expect greater revolutions in the time near at hand than in that of physical chemistry! The value of these for general chemistry will be greater in proportion as the representatives of the same will recognize their task in this: above all to remain upon the *chemical* standpoint and to improve *chemistry* by the application of *physical* modes of thought and experiment. Those, who tried to further the progress of chemistry by the use of physical methods but with insufficient consideration for chemical relations have been led into serious errors. The respect due to work of the highest merit, continued for years, has thus been lessened. Apparently, this has even been overdone, and it is much to be deplored if the interest of chemists for physical chemistry should be diminished because some of its representatives are inclined to overrate the value of their results. He who swims in the midst of high waves is unable at times to see over the crests.

Innumerable also, are the problems which meet us in the domain of organic chemistry.

After the astonishing harvest of synthetical results which has

been reaped here, hardly any problem of synthesis seems unapproachable. Since the artificial preparation of alizarin by Graebe and Liebermann, of indigo by von Baeyer, of conine by Ladenburg, of uric acid by Horbaczewski and particularly by Behrend, since Emil Fischer and Kiliari have elucidated the chemistry of the sugar group and Wallach that of the terpenes, we may well look hopefully for a clearer knowledge of the bodies comprised under the name albumin, and to its synthesis.

But, even such success tends only to render us more modest, since they show us at the same time how narrow are the limits within which chemical synthesis moves. Assuming even that the preparation of albumin had been achieved—how infinitely far we should still be from a conception of the nature of *organized* bodies! Perhaps science is separated by an impassable chasm from the artificial preparation of a simple cell. Such an achievement lies at least beyond the sphere of chemistry.

But shall we really never succeed in sounding the process of *assimilation*, which in spite of its simplicity presents itself to us so enigmatically? Will it be found impossible to prepare artificially in our laboratories from carbon dioxide and water, sugar and starch, a process which nature performs unceasingly in the green parts of plants?

The chemist however, should not step prematurely upon the field of biology, while so many great problems remain untouched in his own peculiar sphere of investigation.

The *method* of research in organic chemistry, in spite of the brilliant successes already recorded, forces us even to-day to confess that only a very minute proportion of known substances is within its reach. In order to isolate an organic substance we are generally confined to the purely accidental properties of *crystallization* or *volatilization*. Have not those thousands of amorphous substances, which cannot be characterized by any chemical property, and which the chemist is forced to lay aside because he is unable either to purify them or to transform them into volatile or crystallizable bodies; have they not the same claim upon our interest as their more beautiful and more manageable comrades?

The most significant progress of organic chemistry does not consist in single discoveries, nor in further expansion of synthetic success. What we want are : *New methods for recognizing the individuality of substances.* The black substances of earthy nature, the innumerable formless and resinous products in the bodies of plants and animals, the coloring matter which gives beauty to flowers, all of these to-day mock our efforts to know them ; they will form a new and inexhaustible field for the prosecution of chemical research, when *methods* shall have been found with which to begin this research.

And as in organic chemistry, so in *mineral chemistry* every step leads to questions, which we have as yet no means of answering. The synthesis of minerals and of rocks has made important progress, it is true, and this as well as the application of the doctrine of structure to the study of mineral species gradually leads to the understanding of their constitution. But we are, as yet, unable to use, in the study of minerals, the method of *analytical decomposition* which has been so successfully used to study the constitution of organic substances, and above all we lack the least knowledge in regard to the *true molecular weight* of minerals.

Quite recently we have been presented with no less than three new and fruitful methods for the determination of the molecular weight, but not *one* of them gives us an indication of the true molecular weight of the most simple oxides, such as silicic anhydride or calcium oxide.

We know to-day very well that silicic anhydride cannot have the formula  $\text{SiO}_2$ , that this must be multiplied by a very large factor ; but of the numerical value of this latter we have no indication. And thus also in mineral chemistry we must aim not exclusively at finding new *facts* but *new methods of research* in the first place, if a period of new discoveries is to be attained in this branch of our science.

But how can we conclude this brief review without mentioning also the *applications of chemistry to the industrial arts*, the progress of which have mainly contributed to spread the splendor of our science most widely ? The infinite variety of the tar colors, surpassing the colors of flowers in number and brightness, is daily



increased by new discoveries. The industry of these forms the most brilliant triumph of purely scientific laboratory work applied to manufactures. This industry in the simplest manner and on the largest scale performs the synthesis of compounds the complex nature of which is indicated by the names they bear. The unscientific man is frightened when a beautiful and brilliant dye is referred to as *Hexamethylmethoxytriamidotriphenylcarbinol*; for the initiated there lies in this unpleasant name a full account of the synthesis and the constitution of the dye.

Industry has learned to derive not only colors but healing medicines also from coal tar. Antipyrin, discovered by Knorr, upon the basis of Emil Fischer's fundamental research upon the hydrazines, brings to thousands suffering from fever, relief at least, if not cure. Let us hope that the time is not far distant when *real* fever curatives, which like the natural alkaloids of the cinchona bark, not only temporarily *suppress* the disease but really *cure* it, may be prepared by synthesis. Until then be patient and do not chide chemistry if, for the time being, she offers only silver instead of gold.

Events in this field of the great chemical industries are significant. We are the witnesses of a great combat taking place between the older process of Leblanc for the preparation of soda and the new one of Solvay called the Ammonia-Soda process. The intelligence and inventive genius of manufacturers have added, under the pressure of this competition, a large number of improvements to the manufacture of sulphuric acid and of soda and new and valuable methods for the preparation of chlorine. Here, more than in any other branch of chemical industry the struggle for existence is fierce.

The manufacture of iron, that most important chemical industry, is transformed by innovations. The imposing changes wrought by the older process of Bessemer, by the new one of Thomas, are they not based purely upon chemical reactions? The grandest application of a complicated chemical reaction to a great manufacture is, perhaps, the dephosphorizing of pig iron by lining the Bessemer converter with basic material, an invention which we owe to Thomas and Gilchrist. From

this again, agriculture derives an advantage in the use of the Thomas slag containing the phosphorus which heretofore rendered iron ore less valuable. This, then, is truly a transformation of stone into bread, similar to the older manufacture of soluble fertilizers from mineral phosphates. Nevertheless, the era of bliss which was prophesied three years ago at the Berlin meeting of naturalists by our illustrious colleague, Ferdinand Cohn, has not yet dawned. He held that all struggles for existence amongst men, arising from want of food, the bread question, will be done away with when chemistry shall have learned to prepare starch from carbon dioxide and water. But since time immemorial the farmer is occupied in this very chemical industry, and it would hardly be great progress if the farm were merely replaced by a chemical factory. But we may reasonably hope that chemistry will teach us *to make the fibre of wood a source of human food*.

Indeed, if we consider how small is the quantity of starch which the grain furnishes us, and further that the wood fibre has exactly the same chemical composition as starch, we see the possibility of increasing the production of food infinitely by solving this problem: *to transform cellulose into starch*.

If this problem were solved we should find an inexhaustible source of human food in the wood of our forests, in grass and even in straw and chaff. The beautiful researches of Hellriegel have recently disclosed the fact, which in former times was disputed, that certain plants transform atmospheric nitrogen into albumin and that this process can be improved by suitable treatment.

The increase of albumin in plants, according to a plan, together with the production of starch out of cellulose—this would in reality signify the abolition of the bread question.

May it some day be granted to chemistry through such a discovery to inaugurate a golden age for humanity.

I have tried to give a review of the most important problems which are set before chemical science. I have mentioned a goodly number, but the short time of one hour permits me to touch but slightly upon the greater ones. There are so many problems before us, which await an immediate solution as to justify what I said in the beginning; that to-day the chemist has no time to

complain because the epoch of a mathematical treatment of his science has not yet arrived.

Nevertheless, the brilliant successes which have been gained, the wonderful results which are immediately within our reach, have not the power to turn our eyes from this final problem.

The Newton prophesied to chemistry by Emil du Bois Reymond, may he appear at a later period; until he comes, may many a generation honorably plow on in the sweat of its brow! We must remember that nature is not understood by us until we are able to reduce its phenomena to simple movements, mathematically traceable.

The time will come, even for chemistry, when this highest kind of treatment will prevail. The epoch in which the foremost impulse of its research was a serenely creative phantasy will then have passed; the joys, but also the pangs and struggles, peculiar to youth, will have been overcome.

Reunited to Physics, her sister science, from whom her ways at present are separated, Chemistry will run her course with firm and unfaltering steps.

## REPORT OF THE COMMITTEE ON INDEXING CHEMICAL LITERATURE.

[*From advance sheets of the Proceedings of the American Association for the Advancement of Science, Vol. 38.*]

The Committee on Indexing Chemical Literature respectfully presents to the Chemical Section its seventh annual report.

During the year just closed three bibliographies have been published by the Smithsonian Institution.

A Table of Specific Gravity for Solids and Liquids. The Constants of Nature, Part I (new edition, revised and enlarged). By Frank Wigglesworth Clark. Washington, D. C., 1888. Smithsonian Miscellaneous Collections No. 659. 8vo, pp. xi, 409.

This volume contains the specific gravities of 5,227 distinct substances and 14,465 separate determinations, being more than twice as many as in the first edition with supplement.

Index to the Literature of Columbium, 1801-1887. By Frank W. Traphagen. Smithsonian Miscellaneous Collections No. 663. Washington, 1888. 8vo, pp. [iv], 27.

This Index contains the threefold arrangement chronological, alphabetical by authors, and subject-matter. The abbreviations of Journal-titles are those adopted by the Committee on Indexing Chemical Literature upon whose recommendation this Index was printed.

A Bibliography of Chemistry for the year 1887 by H. Carrington Bolton. Washington, 1888. Smithsonian Miscellaneous Collections No. 665. 8vo, p. 13.

Prof. Wm. L. Dudley, Vice-President of the Chemical Section of the A. A. A. S., has appended to his address on the Nature of Amalgams an Index to the Literature of the subject which will be printed in the forthcoming volume of the Proceedings of the Toronto meeting.

We record the publication of the following index. Lists of patents relating to Soap and Candles in "Manufacture of Soap and Candles" by Wm. Brannt, Philadelphia, 1889.

Also:—An Index of Researches upon the Production of Ammonia from Atmospheric Nitrogen. By Ezra J. Ware. Pub-

lished in Proceedings Michigan State Pharmaceutical Association, 1888, H. J. Brown, Ann Arbor, Mich., Secretary.

Reports of progress from several volunteer indexers have been received. Dr. Alfred Tuckerman has completed his Index to the Literature of Thermodynamics except a subject-index to which he is putting finishing touches. He has also begun an Index to the Literature of the Chemical Action of Light, a subject suggested by the Chairman of your Committee.

The publication of this annual report is always followed by numerous applications for information, especially with respect to the method of indexing adopted by the Committee. These inquiries we may in some degree anticipate by repeating the statement that this Committee does not prescribe any standard, nor dictate any system for volunteers to follow. Those interested in the work of the Committee would do well to examine the six reports already published, in which will be found suggestions for systematic indexing (1885), a complete list of indexes already printed under the auspices of the Committee (1887), and a list of "Abbreviations of Titles of Chemical Journals," intended to secure uniformity in references (1887).

The choice of subjects for indexing has generally been made by the volunteers themselves; in a few instances only the topics have been suggested by the committee, at the request of co-workers. These subjects, as shown in our reports, cover a wide range in physical, inorganic and organic chemistry; the desirability of procuring indexes to individual elementary substances should not be overlooked by those who contemplate offering aid. A few copies of the Report of 1887 (which includes lists as above) remain, and can be had on application to the chairman, to whom also letters of inquiry may be addressed care of Smithsonian Institution, Washington.

H. CARRINGTON BOLTON, *Chairman*,  
F. W. CLARKE,  
A. R. LEEDS (in Europe),  
A. A. JULIEN,  
JOHN W. LANGLEY,  
ALBERT B. PRESCOTT,  
CHAS. K. WEAD.

REGULAR MEETING, October 4th, 1889.

Vice-President A. C. Hale in the chair.

Mr. Herbert B. Baldwin, of 215 Market Street, Newark, N. J., and Mr. Wm. R. Potter, care of J. P. Shepard & Co., Providence, R. I., were unanimously elected members.

Mr. Martin L. Griffin, of Holyoke, Mass., was proposed for membership.

Mr. C. F. McKenna was elected Recording Secretary in place of Mr. Durand Woodman, resigned.

Messrs. Alsberg, Breneman and Waller were elected a Nominating Committee for the election of officers for the year 1890.

The meeting was then adjourned.

C. E. MUNSELL,

Recording Secretary,

*Pro tem.*

## NOTE ON THE PURIFICATION OF ALCOHOL FOR LABORATORY USES.

BY E. WALLER, PH. D.

Comparatively recently, several papers have appeared on the subject of the reactions of potassium permanganate with alcohols, and the impurities which they may contain.\*

In preparing alcoholic solutions of caustic alkalies, and also of silver nitrate (for fat tests, etc.), I have been annoyed, as have other chemists, by the unsatisfactory character of the solutions bought in consequence of the presence of impurities in the alcohol obtained for laboratory use. I find also that most alcohol of 93 per cent. when kept in tin cans, slowly reacts on the tin, giving, after a while a cloud of  $\text{SnO}_2$ , which is too fine to filter out, and renders purification by distillation necessary. In the light of the results obtained by the writers above alluded to, I have adopted the following method for the purification of my alcohol, on which I ask the criticism of the members of the society.

A convenient amount of the alcohol to be purified is shaken with pulverized potassium permanganate until it assumes a decided color. It is then allowed to stand for some hours, until the permanganate has been decomposed, and brown manganese oxide is deposited. A pinch of pulverized calcium carbonate is then added, and the alcohol distilled at the rate of about 50 c.c. in 20 minutes from a flask provided with a Wurz tube, or one of the Lebel-Heninger pattern. The distillate is tested frequently until about 10 c.c. thereof, when boiled with 1 c.c. of strong (syrupy) solution of caustic soda or potash, gives no perceptible yellow coloration on standing for twenty minutes or half an hour. What distils over after that time is preserved for use.

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\* *Habermann*. *Fres. Ztschr. anal. Chem.* 27, 663. *Rosse*, *ib.* 28, 355.

*Caseneuve*. *Bull. Soc. Chim. (Paris)* [3] 1, 700. See also *Dingl. Polyt. Jour.*, 278, 374.

The first distillates may be added to the small amount remaining in the distilling flask (which should not be driven down to complete dryness), and a fresh portion of purified alcohol recovered.

The rationale of the proceeding appears to be that the permanganate oxides and destroys chiefly the fusel oil, furfural and other compounds of that nature, the acids resulting from the reaction are neutralized by the calcium carbonate added before distillation, and by distilling slowly, the aldehyde at least is concentrated in the first portions of the distillate. Distillation of alcohol containing caustic potash or soda seemed to cause a constant formation of aldehyde. The alcohol thus purified is perfectly neutral, and gives most satisfactory results when used as a solvent for caustic alkalies or silver nitrate, the solutions remaining as colorless as distilled water, even after boiling and standing indefinitely, if properly protected from dust and other external influences.

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### THE EXAMINATION OF COMMERCIAL GLYCERINE.

BY J. H. WAINWRIGHT, PH. B., F. C. S.

The Tariff law of 1883 imposes upon "Glycerine, crude, brown or yellow, of the specific gravity of one and twenty-five hundredths or less at a temperature of sixty degrees Fahrenheit, not purified by distilling or refining," a duty of two cents per pound; and upon "Glycerine, refined" a duty of five cents per pound.

In view of possible attempts to enter, through the Custom House, a partially refined glycerine as the crude article, a sample of every importation of so-called crude glycerine is submitted to the U. S. Laboratory for examination as to whether it is properly invoiced, or is partially or wholly refined; in the latter case it should pay the higher rate of duty. It has been always considered by the chemists at this port that the extent of "refining" properly permissible in a glycerine in order to bring it within the definition of *crude*, is the allowing of impurities to subside by long



standing, or removing them by a process of straining or filtering, and all samples showing evidence of having been treated further than this are reported as *refined* and subjected to the higher rate of duty.

For purposes of classification under the tariff law referred to above *distillation* has always been regarded as the dividing line between crude and refined, and efforts have therefore been made to determine by means of physical and chemical tests whether this process of refining has been employed, since nearly all the glycerine imported as crude is bought by distillers for the manufacture of glycerine to be used in making dynamite (for which purpose distilled glycerine alone is used), and the white C. P. article used for medicinal and pharmaceutical purposes.

I will now call attention to some of the characteristics of crude and refined glycerine. Glycerine, crude, is defined by the tariff [T. I. new, A. 4]), to be "brown or yellow, of the specific gravity of one and twenty-five hundredths, or less, at a temperature of sixty degrees Fahrenheit, not purified by refining or distilling." Crude glycerine is the product obtained directly by stearine candle manufacturers from the saponification or disintegration of their fats and oils, and is a bye-product in the manufacture of soap, being obtained from the waste lyes.

Its specific gravity is usually 1.25, or less, at 60° F., but the gravity of waste lye glycerines sometimes runs much higher owing to the large amounts of chlorides, etc., present.

Its color is yellow, brown or black, but never white, sometimes light yellow, usually medium to dark yellow and often dark brown or black.

It possesses a strong characteristic odor of fatty acids usually disagreeable, sometimes even foetid.

Reaction to litmus paper may be either acid or alkaline, never neutral.

Refined glycerine is usually the product of the distillation of the crude article, the distillation being repeated several times and the resulting glycerine concentrated and further purified by decolorization, etc., according to the uses for which it is intended. Its gravity is usually about 1.25.

Its color ranges all the way from dark brown or even black to white, according to the extent to which the process of distilling or refining has been carried.

If distilled it should have either no odor at all or a more or less burnt odor. This odor in a *distilled* glycerine is highly characteristic and suggests the odor obtained on burning gunpowder. If refined without distillation, as would be shown by other tests, the odor of fatty acids, if any, should be very faint. Distilled glycerine also possesses a characteristic taste faintly suggestive of garlic. This taste, however, as well as the burnt odor, is only exhibited in distilled glycerine of inferior quality.

Reaction neutral or very faintly acid.

In determining the nature of a sample of glycerine a problem is often met with, inasmuch as it is often a matter of great doubt whether a sample has been distilled or not. The following tests, however, I regard as extremely reliable, and, with experience and practice, they afford results which admit of very nice distinction between crude and refined (or distilled) glycerine.

A 10 grm. sample is heated in a tared platinum capsule until it inflames, the source of heat is removed and it is allowed to burn spontaneously; the residue is then weighed and its per cent. calculated. Distilled or refined glycerine will yield from 0. to 0.5 per cent. of "carbonaceous residue," rarely more than 0.5 and never as much as 1 per cent. (unless in the case of an otherwise apparently high grade article it has been adulterated, which would be shown by other tests), whereas crude glycerine frequently yields as high as 10 per cent. I have found the per cent. of "carbonaceous residue" as determined by this test to admit of duplication within very narrow limits.

If desired, a determination of the ash may be made by igniting the "carbonaceous residue."

According to Sulman and Berry (Analyst, 11, 12) the determination of the ash will definitely decide whether the glycerine is crude or distilled; this is somewhat of an error, as it does not necessarily follow that a small proportion of ash alone would indicate that the glycerine has been distilled, since a large proportion of the glycerine manufactured is made directly from fats by

“saponification” with steam, in which case the impurities would necessarily be organic and would be destroyed in the process of incineration, hence, other tests to show the presence of fatty impurities must be employed.

I have frequently found samples yielding as high as three per cent. of “carbonaceous residue” and less than 0.05 per cent. of ash. The proportion of mineral matter, however, affords a good indication of the character of the sample, since, in refined glycerine, the ash is never higher than 0.2 per cent. and rarely as high as 0.1, whereas, in crude glycerine made from soaps, lyes and by other processes of saponification, the ash frequently runs as high as 14 per cent.

If deemed desirable, an examination of the ash may be made, this also will often afford an indication of the source of manufacture from which the glycerine was obtained (Allen’s Com. Org. Anal., 2d ed., 2, 297). Of all the other tests which are recommended for the examination of glycerine the two most important are those made with solutions of silver nitrate and basic lead acetate in distilled water, the former being a two per cent. solution and the latter being made by adding 10 grams. of C.P. lead acetate and 8 grammes of litharge to 500 c. c. distilled water, boiling for some time and filtering. The tests are made as follows :

*The silver nitrate test.*

Dissolve 5 c. c. of the sample to 20 c. c. distilled water in a large test tube and add 5 c. c. silver solution, shake, allow to stand at rest for one hour. In refined glycerine a darkening of the solution may occur, with even a slight reduction of silver, after standing some time; it will be quite heavy if allowed to stand long enough, even in highly refined samples, but if it is not quite heavy at the end of one hour the result may safely be considered an indication of refined glycerine. In crude glycerine a considerable precipitation takes place, usually at once, and is nearly always *flocculent*. The precipitate may be of any color from black to white, according to the nature of the impurities present.

*The lead test.*

This test is made by adding to the lead solution in a large test tube, its own volume of a solution containing equal volumes of

the sample and distilled water, and shaking and allowing to stand at rest for one hour, as in the silver test. Refined glycerine will remain unchanged or will show a slight precipitation or cloudiness, but never a *flocculent* precipitate, even on standing for a long time, whilst in crude glycerine there will always be more or less of a flocculent precipitate.

In applying these tests it is *never* safe to rely on either of them *alone*, as it will frequently happen that a sample will be met with which will stand one test and not the other; however, if it will not stand *both* of these tests it is perfectly safe to call it crude, and, with some experience, a fair idea of the *value* of the sample may be obtained. By boiling, the tests may be greatly hastened, although this is not recommended except in extremely doubtful cases, as the test thereby becomes much more delicate.

If deemed desirable, other tests may be made, and among them the following will be found useful:

The addition of an equal volume of distilled water. Refined glycerine will remain clear. In *crude* glycerine if much oil or fat be present they may be separated from the glycerine in this manner:

Ammonia.—*Refined*, no change; *crude*, precipitate indicates presence of *iron* and *alumina*.

Ammonium Oxalate.—*Refined*, no change; *crude*, precipitate indicates *lime* salts.

Barium Chloride.—*Refined*, no change; *crude*, precipitate indicates *sulphates*.

Nitrogen Peroxide (Gas).—*Refined*, no change; *crude*, curdling indicates *fatty impurities*.

Fehling's Solution.—*Refined*, no change; *crude*, shows the presence of *glucose*, etc.

For other tests recommended for the examination I would refer to the very able paper of Messrs. Sulman and Berry (*Analyst*, 11, 12 and 34) and to Allen's *Com. Org. Anal.* (2d ed., vol. 2, 292 et seq.).

With a fair amount of experience a discrimination between crude or raw and refined or distilled glycerine will readily be accomplished by means of the foregoing tests and, moreover, a fair

idea as to the quality of the sample may be obtained, and it may be ascertained beyond a doubt whether it is fit for the manufacture of nitro-glycerine for which so much of the refined glycerine of commerce is used.

UNITED STATES LABORATORY,

New York, December 6th, 1889.

### THE NOMENCLATURE AND NOTATION OF ALKALOIDAL SALTS.

BY S. W. WILLIAMS.

Now that the U. S. Pharmacopœia is about to be revised, it seems eminently proper that the American Chemical Society should recommend a system of nomenclature and notation for alkaloidal salts more consistent than that adopted by the last Committee of Revision.

Four names and four formulas fairly representative of the terminology and symbolic representation of salts formed by acids, with alkalies and alkaloids, should be sufficient to demonstrate that a wider divergence from consistency could hardly have been attained :

<i>Pharmacopœial Name.</i>	<i>Pharmacopœial Formula.</i>
Ammonium bromide.	$\text{NH}_4 \text{ Br.}$
Quinine hydrobromate.	$\text{C}_{20} \text{ H}_{24} \text{ N}_2 \text{ O}_2 \text{ H Br.}$
Potassium sulphate.	$\text{K}_2 \text{ S O}_4$
Quinine sulphate.	$(\text{C}_{20} \text{ H}_{24} \text{ N}_2 \text{ O}_2)_2 \text{ H}_2 \text{ SO}_4.$

Note as inconsistencies :

1. Writing a salt as a hydrobromide and naming it a hydrobromate.
2. Calling one salt of hydrobromic acid a hydrobromate and another salt of the same acid a bromide.
3. Recognizing in the name of one salt the unreplaced hydrogen of the combining acid and ignoring the same unreplaced hydrogen in another.

4. Making the name sulphate applicable to both metallic and alkaloidal salts of sulphuric acid, while the term bromide is made inapplicable to both metallic and alkaloidal salts of hydrobromic acid, practically the same difference existing between metallic and alkaloidal salts in one case as in the other.

5. (Should the ammonium theory be offered in partial explanation): Incorporating the hydrogen of the combining acid with the base in the case of  $\text{N H}_4 \text{ Br}$  and not doing so in the case of



In my opinion to prove quinine hydrobromate a correct term requires evidence that a "bromide" is a "bromate." To make quinine sulphate anything more than a defective name (correct, however, as far as it goes). requires for consistency that the notation be changed from



this change resulting in the second inconsistency of calling  $\text{C}_{20} \text{H}_{24} \text{N}_2 \text{O}_2$  (the free alkaloid capable of individual existence) by the same name as that given to  $\text{C}_{20} \text{H}_{25} \text{N}_2 \text{O}_2$ , a hypothetical base as yet, so far as the writer knows, not proved to be capable of standing alone.

If accepted notation is to stand as it is, the writer would argue for such terms as hydrobromide and hydrosulphate (obsolete for sulphide) as accurately descriptive of the formulas given by the Pharmacopœia and authorities generally, these terms to be abbreviated for convenience, and perhaps reasonable conservatism in the case of oxyacid salts, to "bromide" and "sulphate."

The only change in notation which seems to commend itself at all is the incorporation of the unreplaced hydrogen of the combining acid with the hydrogen of the base—a change based upon the ammonium theory. The question here presents itself: Is the theory sufficiently well established to warrant such alteration? Do we *know* even that " $\text{N H}_4 \text{ O H}$ " is more than a mere solution of  $\text{N H}_3$  in  $\text{H}_2 \text{ O}$ ?

Several years ago the writer, then engaged editorially on a weekly pharmaceutical journal, endeavored to bring the subject of

correct names for alkaloidal salts prominently before pharmacists, and many members of this society then joined in the resulting discussion with considerable interest. Of twenty-seven chemists who gave their opinions but four favored at all the terminology adopted by the Pharmacopœia for the alkaloidal salts of alkaloids containing hydracids. The principal "argument" advanced by the small minority was practically: "It is correct because long ago adopted and now employed," substantially the same thing as saying that chemical terms are mere conventionalities.

Our objections at the time were made principally against such terms as hydrochlorate, hydrobromate and hydriodate, claiming the greater accuracy of the names hydrochloride, hydrobromide, hydriodide, etc. The latter terminology, though practically unrecognized in the trade, and in pharmaceutical and even most chemical literature, had nevertheless been adopted by the English Chemical Society and has now the support of our own organization. It is needless to argue here the desirability of making pharmacopœial terminology not only consistent with itself but so far as practicable with the language of chemistry. It would certainly have been no greater change to substitute the term hydrochloride (signifying an "addition product" with H Cl) for "muriate" (U. S. P., 1870), than to impose a name of exactly the same length which indicates an "addition product" with chloric acid, the prefix "hydro" suggesting unreplaced hydrogen in both cases.

Claiming no consideration for his personal views, the writer would however ask a careful perusal of the following brief extracts from letters \* written by chemists who may be taken as fairly representative authorities:

[The example taken for discussion is the salt formed by cocaine with hydrochloric acid.]

Professor Wolcott Gibbs (Harvard):

\* \* "I should myself prefer to call it the *hydrochloride* of co-

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\* The letters will be found in full in reprints from the "Weekly Drug News," '84-'85, published in pamphlet form by the "Druggists' Circular," 72 William St., New York. The book, entitled, "Cocaine Hydrochloride as the Name of the Salt formed by Cocaine with Hydrochloric Acid and a Discussion of the Nomenclature of Alkaloidal Salts in General," may be obtained from the publishers.

caine, adopting the nomenclature proposed some years ago in England, I believe by Prof. Foster."

Professor John Howard Appleton (Brown):

"My personal feeling is that the new local anæsthetic had better have the word *hydrochloride* than hydrochlorate as a part of its name. \* \*

Professor A. A. Breneman (late of Cornell University), [after remarking upon the propriety of applying the ammonium theory to alkaloidal salts, and calling the salt coconium chloride]:

"My own preference, therefore, would be for the term 'hydrochloride of cocaine,' or rather, in accordance with present usage, *cocaine hydrochloride*, to designate the new remedy and as a typical name for compounds of this class. I cannot think that usage in favor of the term 'hydrochlorate' is yet so firmly established as to forbid a change so desirable."

Prof. F. W. Clarke (Smithsonian Institution):

"I prefer to use either 'hydrochlorate' or 'hydrochloride.' 'Chloride' is bad, because it ignores the hydrogen, which is essential to the compounds. \* \* \* \* Probably the terms sulphate, hydrochlorate, etc., are, all things considered, best; for, after all, these names are mere conventionalities." \* \*

Prof. John M. Maisch (Philadelphia College of Pharmacy):

\* \* "As far as my personal preference is concerned, I am rather in favor of *hydrochloride*, etc., as a good descriptive term for salts containing the hydrogen compounds of halogens; therefore: hydrobromide, hydrocyanide, etc., is analogous to chloride for compounds containing Cl."

Prof. P. T. Austen (Rutgers College):

"I am glad to see that you are endeavoring to correct the popular error into which some writers have fallen in using the term cocaine hydrochlorate. The addition compound of cocaine with hydrochloric acid is properly called cocaine hydrochloride. You will find this matter of nomenclature very exactly stated in the Nineteenth Instruction to Abstractors published by the late Henry Watts, F. R. S., F. C. S., in the Journal of the English Chemical Society (1879, vol. 35, p. 281). \* \* The use of the name cocaine chloride is also wrong, since this would signify that



the salt was formed by the replacement of the atom of hydrogen in hydrochloric acid by cocaine, which is not the case."

Prof. Ira Remsen (Johns Hopkins' University), [after commenting upon the analogy between ammonium and alkaloidal salts] :

"The salt is therefore the chloride of this hypothetical substance, and, to give it a systematic name analogous to that of ammonium chloride, we should be obliged first to find a name for this hypothetical substance. We might, for example, call the latter *cocainium*. Then the salt would be namely *cocainium chloride*. In short the salt is a chloride ; but, to avoid the necessity of giving a special name to the substance with which the chlorine is combined, it appears better to adopt a generic name for all similar salts, and, as they all contain this extra hydrogen, which is the cause of the trouble, the name best suited to call attention to the fact is, perhaps, *hydrochloride*. \* \* \* Such names as *hydrococaine chloride*, *hydroquinine nitrate*, etc., would be the best, and, save that they are new, they are entirely unobjectionable."

The late Prof. Henry B. Parsons (then editor Druggists' Circular) :

"\* \* \* As to the respective merits of the terms *hydrochlorate* and *hydrochloride*, as applied to salts of alkaloids, it may be stated—

1st. The usage of the English and U. S. Pharmacopœias is on the side of the termination *ate*.

2d. Some of the best chemical writers, however, use the more correct termination *ide*. \* \* \* As the termination *ide* is proper in connection with mineral salts, and as no confusion can result from its adoption in naming salts of alkaloids, while uniformity will be promoted thereby, it seems to me preferable to write *cocaine hydrochloride* in place of cocaine hydrochlorate."

Prof. W. H. Greene (Central High School, Philadelphia):

"\* \* \* The word hydrochlorate—a direct translation of the French *chlorhydrate*—is, without doubt, objectionable for a compound which is not in any manner a hydrate or a chlorate. \* \* \* In conclusion, nomenclature should be as concise and simple as is consistent with precision. If, then, *cocaine chloride* is not

sufficiently definite, let it be *cocaine hydrochloride*, but not hydrochlorate."

Dr. D. K. Shute (Washington, D. C.):

"\* \* \* Your argument against the term 'hydrochlorate' is very conclusive, at least as far as modern scientific chemistry is concerned. I cannot agree with you, however, that 'hydrochloride' is more correct than *chloride* and, therefore, preferable to it." [This writer goes into an argument for the term "chloride" based upon the ammonium theory.]

Professor A. B. Prescott (Michigan University):

"\* \* \* You recommend that the change in the word-ending for these salts, from -ate to -ide, a change already made and being made in the language of chemists be adopted in the language of pharmacists. It is well that the use of terms in pharmaceutical commerce shall not fall far behind the use of terms in chemical science. In fact, the closer are all the relations between applied science and pure science, the better it is for the progress of each. The world of manufacture and of use stimulates and is strengthened by the world of investigation and discovery." \* \* \*

Prof. S. W. Johnson (Yale University):

"\* \* \* The name hydrochlorate of cocaine is correct as is also the term hydrochlorate of ammonia. These are both correct because chemists long ago adopted and now employ them." \* \*

Prof. Sidney A. Norton (Ohio State University):

"Your editorial seems to fill the bill, and to show that cocaine hydrochloride is the best name." \* \* \*

Prof. H. A. Mott (New York):

"Keep on agitating the question of scientific nomenclature.  
\* \* \* The compound  $C_{17}H_{21}NO_4 \cdot HCl$  can only be correctly represented by the name *Cocaine Hydrochloride*; the ending 'chlorate' is very misleading and should not be employed."

Wm. Rupp F. C. S., (New York), [explaining the combination of an acid as a whole with an alkaloid in virtue of a gain in quantivalence of two bonds by the nitrogen, and commenting on the application of the ammonium theory to salts of the alkaloid, morphine for example]:

"\* \* \* If this were done the analogy with the ammonium

compounds would be complete, and the term *morphonium chloride* would be correct ; whereas nothing will justify the term *morphine chloride*." \* \*

Prof. Maurice Perkins (Union College):

"\* \* I think the termination 'ide' much better than 'ate,' for this latter would seem to indicate that the acid radical contained oxygen, which it does not."

Prof. J. P. Remington (Philadelphia College of Pharmacy):

"\* \* My own view is, that the combinations of the hydracids with alkaloids are properly termed *hydrochlorides*, etc.; that chloride bromide, iodide, etc., are proper terms to use, when halogen acids combine with metals, and the hydrogen *is* replaced, is now generally accepted ; what more rational view can be taken than to indicate the *presence* of hydrogen, in the compounds wherein the hydrogen has *not* been replaced, by the addition of the *descriptive prefix hydro*." \* \*

Prof. N. T. Lupton (Vanderbilt University):

"\* \* My personal preference is to call such compounds chlorides and not hydrochlorides, but as stated above, I follow the usage of the journal of the Chemical Society of England and call the compound formed by the action of hydrochloric acid on cocaine, cocaine hydrochloride."

Prof. George T. Barker (University of Pennsylvania), [after reviewing the history of the terms in question and commenting on the ammonium theory]:

"\* \* My judgment, therefore, is : 1st, that the term 'hydrochlorate' is entirely inadmissible having neither precedent, analogy or sound reason in its favor ; 2d, that the term 'hydrochloride' is anomalous and unscientific, though preferable to 'hydrochlorate;' and 3d, that, in accordance with the spirit of the Lavoisierian nomenclature, the term 'cocainum chloride' is to be recommended as having the most points in its favor."

Prof. W. G. Levison (Cooper Union) :

"\* \* It might be interesting to subject the cocainum compound to electrolytic examination, though negative results would probably be obtained as in the case, so far as I know, of the other alkaloidal hydrochlorides. Until, however, a radical ( $C_{17}H_{22}NO_4$ )

is in some way demonstrated to form, the noncommittal name of cocaine hydrochloride seems least objectionable."

Dr. A. B. Lyons (Detroit):

"\* \* Now, the question has narrowed itself to this; is it best, all things considered, to distinguish the ammonia cocaine ( $C_{17}H_{21}NO_4$ ) from the base radical,  $C_{17}H_{22}NO_4$ ? If so, the distinction can best be made as in the case of ammonia itself, by simply changing the *a* of the (Latin) name into *um*. Our compound will therefore be called, for precision, cocainum chloride. \* \* \* I would give the name cocaine to the radical which, by its direct union with chlorine forms the chloride—for I believe that Cl is monad in this compound as in other chlorides—and, if necessary, would distinguish as cocaine alkaloid the compound ammonia commonly designated simply as cocaine."

Prof. F. B. Power (University of Wisconsin):

"\* \* We know that many alkaloids are capable of absorbing hydrogen and forming 'hydro' compounds, and to such addition products this expression should be reserved. Should cocaine be found to possess this property its salt with HCl would then be a *hydro*-cocaine, hydrochloride, or hydrochlorate. There seems to me but little doubt regarding the propriety of the term hydrochloride as opposed to hydrochlorate." \* \* \*

Prof. Charles A. Doremus (Bellevue Medical College):

"\* \* I prefer the term cocaine hydrochloride, though the salts of the alkaloids with hydrochloric acid are termed hydrochlorates by many eminent chemists, and have therefore the sanction of authority. There would be no objection to either the term 'cocanium chloride' or 'hydrococaine chloride.'" \* \*

Prof. Oscar Oldberg (Chicago College of Pharmacy):

"\* \* It seems to me important not to overlook the fact that the nomenclature of the compounds formed by alkaloids with hydr-acids must be in perfect harmony with the names of alkaloidal salts of the oxy-acids. It is at least consistent to say cocaine chloride when we say morphine sulphate. \* \* \* Professor Remsen's suggestion is, to my mind, the only proper one to accept."

Dr. Lawrence Wolff (Philadelphia):

"\* \* I am in favor of the term 'cocaine chloride' modified from the term 'hydrococaine chloride,' as proposed by Prof. Ira Remsen." \* \* \*

Prof. John Attfield (London, Eng.) :

"\* \* Expediency may, and I think does, suggest the name 'hydrochlorate of cocaine,' and consistency, as far as it goes, supports expediency; but what philological correctness points to I cannot say. \* \* Remember that in our choice of such terms we are not guided by the laws of nature, but by a jumble of conventions. There is much to be said for the words of which 'hydrochloride' is an example, and nothing but good to all interests concerned is likely to come out of a discussion on chemical nomenclature in your columns."

Prof. J. U. Lloyd (Cincinnati, O.) :

"\* \* 1st. If an alkaloid unites with HCl so that the hydrogen is separated from the chlorine, which then acts as a radical, according to present usage the compound should properly be called a *chloride*.

2d. If the combination HCl is known under the name of hydrochloric acid, and, if it is the custom to call compounds of this acid in which the entire undecomposed acid is involved by the name *hydrochlorate* (as I think most writers now use it), then the union of cocaine and HCl could be called *hydrochlorate of cocaine*.

3d. If the combination HCl is regarded as hydric chloride, or chloride of hydrogen, and the undecomposed compound HCl is supposed to unite with the alkaloid, I do not see why the term cocaine hydrochloride is not in conformity with our ordinary nomenclature." \* \*

Space will not admit of doing anything like justice to the writers of the letters quoted from. It will be observed from the foregoing opinions that there are *many* arguments against the pharmacopœial terminology and practically *none* for it. A change is therefore clearly indicated. What shall the change be?

S. W. WILLIAMS.

*Seabury Pharmacal Laboratories,  
East Orange, N. J.*

REGULAR MEETING, Nov. 1st, 1889.

President C. F. Chandler in the chair.

The minutes of the October meeting were read, as also those of the directors' meeting held October 9th.

Mr. Martin L. Griffin, of Holyoke, Mass., was elected as member.

The Chair read a communication addressed to him by the Mayor of the City calling upon those interested in scientific and educational matters for aid in promoting the International Exposition of 1892. Upon motion of Mr. Wainwright, the matter was made the order for the next meeting.

Mr. Rupp read a letter from Prof. Breneman, and also reported the nominations of the committee. They were as follows :

Corresponding Secretary : M. Alsberg.

Recording Secretary : C. F. McKenna.

Treasurer : J. H. Stebbins, Jr.

Librarian : W. Rupp.

Curators : W. H. Kent, J. B. Herreshoff, A. H. Sabin.

Committee on Papers and Publications : A. C. Hale, A. A. Breueman, J. F. Geisler.

Committee on Nominations : H. Endemann, A. P. Hallock, T. S. Gladding, C. A. Doremus, A. Eimer, T. D. O'Connor.

Board of Directors : M. Alsberg, J. F. Geisler, M. Waldstein, H. Endemann, W. H. Kent, T. D. O'Connor, L. H. Friedburg, C. F. Chandler, W. Rupp.

On motion, the report of the Committee on Nominations was accepted and the nominations were adopted.

Letters were read by the Secretary from Dr. Mendeleeff, of the University of St. Petersburg, acknowledging his election as an

honorary member of the Society, and from Prof. C. E. Munroe on the subject of reorganization of the Society.

A discussion upon the present state of the Society was then opened. Dr. Alsberg remarked upon the condition of the finances as brought to light at the last directors' meeting. Remarks upon these subjects were made by many members.

The action of the Chemical Section of the American Association for the Advancement of Science was reported by Prof. Vanderburgh and Prof. Nason, both of whom were present.

Dr. Waller moved that the members present be requested to state how much they would pledge for the next year in the way of papers, money and attendance.

On motion of Mr. Geisler a committee of five was appointed to canvas the whole membership of the Society upon the subject. Messrs. Geisler, Doremus, Wainwright, Kent and Waller were appointed by the Chair.

After some remarks by Dr. Kent on amending the By-laws, and by Mr. Wainwright on reorganization, the meeting was adjourned.

CHAS. F. McKENNA,

Recording Secretary.

## ANALYSES OF SOME MINERAL WATERS FROM TEXAS.

By C. F. CHANDLER AND E. WALLER.

In the Bulletin of the United States Geological Survey No. 32 (Mineral Springs of the United States), among the analyses of Texas waters, appear some partial analyses, with a reference to C. F. Chandler as analyst. The results there quoted were no doubt communicated by the proprietors of the springs, and represent the kind of examination requested by them. Those waters, however, and a few others examined about that time, were sufficiently interesting to induce us to make more extended examinations, which we think may be worthy of record.

The presence of weighable quantities of manganese in the most of these waters, as well as in some cases traces of zinc and copper, first attracted our attention as being not very common constituents of mineral waters. Indeed we have heard the opinion expressed that zinc and manganese were unheard of. But S. Dana Hayes reports the presence of 18.831 grains  $\text{Zn SO}_4$  in a water from Mercer Co., W. Va. (Am. Chem., V., 277). Prof. Hardin's report on the Rockbridge Alum Springs of Virginia shows weighable quantities of Mn, Zn and Cu in those waters (Am. Chem., IV., 247), and Prof. Mallet finds Mn and Cu in the Capon Springs of W. Va. We have also found Mn in other mineral waters from Virginia, and a search through Dr. Peale's collection of statistics (Bulletin No. 32 above referred to) shows that the presence of manganese is recorded in waters from some 36 different localities, representing fifty or more springs. Many of these are waters from Pennsylvania, reported by Dr. Genth, but the element has been found by other analysts in waters from many other States. It is also reported as a constituent in several European waters, *e. g.*, the Vosges Mountains (C. Rend., Mar., 1880), the Pyrenees, Garegon (C. Rend., LXXXIV., 963), Birresborn (Berichte IX., 987), Bad Helmstedt (Jour. Pr. Chem., 1873, No. 5), etc.



Manganese no doubt has a therapeutical value, but on that point we do not feel competent to express a decided opinion.

The waters have been named according to the places from which they were sent. With the exception of the Houston water, which was alkaline, the waters were neutral, no free acid being discernable by tests with methyl orange or by any other means. In the Waco and Kosse waters, the acid present was insufficient to satisfy all of the bases present, leading to the inference that either basic salts were present, or, what we think is more probable, that the alumina or ferric oxide was combined with some organic acid or compound of unknown composition. A similar case is on record—Orchard Alum Springs of England, Dr. Thresh (*Chem. News*, XLVI., 226).

As to ferric compounds, in many cases the suspicion comes into the mind of the analyst, that oxidation may sometimes have occurred after drawing the water from the spring, but he can only report the conditions which he actually finds.

We give the details of actual quantities of bases found, as well as the probable combinations.

(Parts per 100,000.)

	Wootan No. 1.	Wootan.	Hearne.	Waco.	Bryan.	Kosse.	Houston
Na <sub>2</sub> O .....	22.959	-----	34.163	12.405	5.668	1.602	30.631
K <sub>2</sub> O .....	3.589	-----	1.918	1.322	1.257	-----	4.380
Li <sub>2</sub> O .....	-----	-----	-----	-----	-----	-----	trace.
Mg O .....	22.480	30.000	45.607	18.569	16.036	5.616	26.339
Ca O .....	43.230	46.470	71.943	44.125	32.477	9.209	55.794
Ba O .....	-----	-----	-----	-----	-----	-----	trace.
Zn O .....	-----	-----	-----	-----	trace.	-----	-----
Mn O .....	0.980	-----	1.350	0.540	0.660	-----	0.167
Fe O .....	3.287	25.81	25.455	20.801	25.922	1.700	-----
Fe <sub>2</sub> O <sub>3</sub> .....	1.696	-----	6.640	6.209	5.347	-----	0.175
Al <sub>2</sub> O <sub>3</sub> .....	2.092	-----	6.784	0.650	7.330	6.539	0.185
Cu O .....	-----	-----	-----	-----	-----	-----	-----
Cl .....	41.739	60.800	27.886	12.977	6.849	1.834	102.200
SO <sub>2</sub> .....	102.320	135.900	255.430	127.238	134.212	44.940	29.243
P <sub>2</sub> O <sub>5</sub> .....	-----	-----	0.140	-----	-----	-----	0.020
Si O <sub>2</sub> .....	5.63	5.550	4.420	5.485	11.055	5.20	2.290
Loss by ig'n	16.50	21.000	25.000	6.500	24.30	8.800	32.000
Res. Evap'n	256.70	340.200	530.000	270.500	317.00	88.680	275.000

(Parts per 100,000.)

	Wootan No. 1.	Hearne.	Waco.	Bryan.	Kosse.	Houston.
Na Cl .....	43.819	45.934	21.887	10.694	8.028	57.686
Mg Cl <sub>2</sub> .....	20.732	-----	-----	-----	-----	62.423
Ca Cl <sub>2</sub> .....	-----	-----	-----	-----	-----	82.257
Mn Cl <sub>2</sub> .....	-----	-----	-----	-----	-----	0.800
Cu Cl <sub>2</sub> .....	-----	-----	-----	-----	-----	trace.
Na <sub>2</sub> SO <sub>4</sub> .....	-----	22.463	2.451	-----	9.700	-----
K <sub>2</sub> SO <sub>4</sub> .....	6.644	3.547	2.445	2.325	-----	8.108
Mg SO <sub>4</sub> .....	41.25	136.822	55.708	48.108	16.848	-----
Ca SO <sub>4</sub> .....	104.99	174.720	107.160	78.872	22.365	43.375
Zn SO <sub>4</sub> .....	-----	-----	-----	trace.	-----	-----
Mn SO <sub>4</sub> .....	1.979	2.871	1.148	1.404	-----	-----
Fe SO <sub>4</sub> .....	6.939	53.739	43.912	54.735	3.526	-----
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .....	4.238	16.602	-----	13.367	-----	-----
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .....	6.976	22.624	2.168	24.440	5.745	-----
Na <sub>2</sub> HPO <sub>4</sub> .....	-----	0.281	-----	-----	-----	0.041
Li HCO <sub>3</sub> .....	-----	-----	-----	-----	-----	trace
Ca (HCO <sub>3</sub> ) <sub>2</sub> .....	-----	-----	-----	-----	-----	62,575
Ba (HCO <sub>3</sub> ) <sub>2</sub> .....	-----	-----	-----	-----	-----	trace.
Fe (HCO <sub>3</sub> ) <sub>2</sub> .....	-----	-----	-----	-----	-----	0.389
Si O <sub>2</sub> .....	5.630	4.420	5.485	11.055	5.400	2.290
Fe <sub>2</sub> O <sub>3</sub> .....	-----	-----	6.209	-----	-----	-----
Al <sub>2</sub> O <sub>3</sub> .....	-----	-----	-----	-----	4.816	0.185
Loss by ig'n .....	16.50	25.00	6.500	24.300	3.800	32.00
Res. Evap'n .....	256.70	530.30	270.500	317.00	88.680	275.00

(Grains per U. S. gallon of 231 cu. in.)

	Wootan No. 1.	Hearne.	Waco.	Bryan.	Kosse.	Houston.
Na Cl .....	45.263	26.788	12.469	6.236	1.763	33.641
Mg Cl <sub>2</sub> .....	12.090	-----	-----	-----	-----	36.404
Ca Cl <sub>2</sub> .....	-----	-----	-----	-----	-----	18.812
Mn Cl <sub>2</sub> .....	-----	-----	-----	-----	-----	0.175
Cu Cl <sub>2</sub> .....	-----	-----	-----	-----	-----	trace.
Na <sub>2</sub> SO <sub>4</sub> .....	-----	13.100	1.429	-----	5.657	-----
K <sub>2</sub> SO <sub>4</sub> .....	3.875	2.068	1.426	1.486	-----	4.728
Mg SO <sub>4</sub> .....	24.056	79.792	32.488	23.056	9.825	-----
Ca SO <sub>4</sub> .....	61.228	101.893	62.494	45.997	13.043	25.296
Zn SO <sub>4</sub> .....	-----	-----	-----	trace.	-----	-----
Mn SO <sub>4</sub> .....	1.154	1.674	0.670	0.819	-----	-----
Fe SO <sub>4</sub> .....	4.047	31.340	25.607	31.920	2.056	-----
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .....	2.472	9.861	-----	7.795	-----	-----
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .....	4.068	13.192	1.264	14.230	3.350	-----
Na <sub>2</sub> HPO <sub>4</sub> .....	-----	0.164	-----	-----	-----	0.024
Li HCO <sub>3</sub> .....	-----	-----	-----	-----	-----	trace.
Ca (HCO <sub>3</sub> ) <sub>2</sub> .....	-----	-----	-----	-----	-----	36.492
Ba (HCO <sub>3</sub> ) <sub>2</sub> .....	-----	-----	-----	-----	-----	trace.
Fe (HCO <sub>3</sub> ) <sub>2</sub> .....	-----	-----	-----	-----	-----	0.227
SiO <sub>2</sub> .....	3.233	2.578	3.199	6.447	3.149	1.335
Fe <sub>2</sub> O <sub>3</sub> .....	-----	-----	3.631	-----	-----	-----
Al <sub>2</sub> O <sub>3</sub> .....	-----	-----	-----	-----	2.809	0.103
Loss by ig'n .....	9.632	14.579	3.791	14.171	1.924	18.663
Res. Evap'n .....	149.702	309.260	157.488	175.945	52.369	157.750

## COMPARATIVE RESULTS IN THE ANALYSIS OF FATS.

BY RUSSELL W. MOORE, A. M., M. SC.

Having had occasion to employ extensively the modification of the Reichert process proposed by Dr. E. Waller (*J. Am. Chem. Soc.*, 8, 155), it has occurred to the writer that some comparative results with the Hehner or wash process would be of sufficient interest to warrant publication.

The modification, or rather extension of the Reichert process is conducted as follows: The Reichert process is strictly followed out; two and five-tenths grammes of fat are saponified with one gramme of caustic potash, and fifty c. c. of seventy per cent. alcohol. The alcohol, after the saponification is complete, is entirely driven off, the last portions being removed by a current of air and the resulting soap is dissolved with the aid of heat, in fifty c.c. of water, and decomposed with twenty c.c. of dilute sulphuric acid (1:10). The flask is now attached to a condenser, preferably of the well known upright glass worm shape furnished with a bulb tube to prevent mechanical carrying over of the acid, and exactly fifty c.c. are distilled off and titrated with  $\frac{N}{10}$  NaOH. The Reichert figure is thus obtained, and a certain portion of the volatile fatty acid has been removed. Fifty c.c. of water are added to the contents of the flask, the distillation is repeated and the distillate titrated, and this same course is continued until a practically neutral distillate of 50 c.c. is obtained, that is, one requiring one-tenth of one c.c. of  $\frac{N}{10}$  NaOH, or less, for neutralization. The total amount of acidity of all the distillates is now calculated as butyric acid, and the total per cent. of volatile fatty acid is thus obtained.

The insoluble acids now remain in the flask and the bulb tube or adhere to the sides of the condenser or filter used to filter the

distillate. The portion in the bulb tube and condenser is rinsed into a small flask with a little hot alcohol, and that in the flask is allowed to become solid. The liquid underneath, containing sulphuric acid, potassium sulphate and glycerine, is poured off through the filter that received the original distillate. The fatty acids are then treated with hot water several times, allowing them to cool into a cake before pouring the wash water through the filter. When the wash water shows no reaction for sulphuric acid the washing is complete. Three washings of about 100 c. c. each usually suffice for this purpose. The rinsings of the condenser are now added to the insoluble fatty acids, the filter is exhausted with hot alcohol to remove adhering fatty acid, the alcohol is expelled and the contents of the flask are dried to constant or slightly increasing weight at 105°C. The per cent. of insoluble fatty acids can then be calculated.

Bumping during distillation can be avoided by using spirals of coarse platinum wire; these can be weighed with the flask, and require no further attention.

A blank test of the reagents used should also be made and any acidity yielded by them in the distillate allowed for.

The method conducted as above furnishes:

- (1.) The Reichert figure.
- (2.) The soluble fatty acids.
- (3.) The insoluble fatty acids.

The advantages claimed for this method are as follows:

(1.) A combination of the two most valuable and reliable methods, the Reichert and the elaborated Hehner into one.

(2.) Greater ease and rapidity of manipulation than the Dupré method.

(3.) Avoidance of loss of insoluble fatty acids due to transfer of the fatty acids from the flask in which the fat was originally weighed. The filter used is a small one and can easily be exhausted with hot alcohol.

(4.) Necessity of only one standard solution instead of four, as in the Dupré process. The  $\frac{N}{10}$  Na OH is a very permanent solution and the use of alcoholic K OH which is subject to daily and even hourly change is avoided.

(5.) Accuracy of results. This is shown by the following figures :

BUTTER.

	WASH PROCESS.		WALLER'S PROCESS.	
	Per Cent. of Soluble Acids.	Per Cent. of Insoluble Acids.	Per Cent. of Soluble Acids.	Per Cent. of Insoluble Acids.
Jersey Butter .....	6.37	87.67	6.30	87.54
Rancid Butter.....	6.53	88.48	6.49	88.56
Dairy Butter, November..	5.42	87.71	5.61	87.74
Holstein Butter.....	5.11	89.00	5.28	88.96
Native Butter .....	5.76	87.09	5.80	87.10
Devon Butter.....	6.86	87.79	6.86	87.76

OLEOMARGARINE.

No. 1124 .....	0.16	95.64	0.16	95.50
" 135 .....	0.27	95.68	0.28	95.40
" 492 .....	0.69	94.96	0.67	94.92
" 137 .....	0.18	95.98	0.14	95.94
" 999 .....	0.36	95.12	0.28	95.14
" 686 .....	0.20	96.02	0.23	96.00
" 493 .....	1.68	93.52	1.51	93.78

OILS.

Olive Oil.....	0.34	94.82	0.28	94.58
Mustardseed Oil .....	-----	95.66	-----	95.61
Porpoise Jaw Oil .....	16.98	71.93	16.70	71.98
Cocoanut Oil .....	7.00	80.87	4.92	83.12

The results above given all show a satisfactory agreement with one exception, and the two processes may be considered to give practically identical results. The exception in this case is coconut oil. It will be noticed that the sum of the fatty acids by both processes is practically the same, but that more soluble acid is extracted by the wash process than by distillation. The results

obtained by both of the processes on this oil were far from satisfactory. In the wash process 2.495 grammes of fat were used and twenty-five washes of the fatty acids were made, each consisting of 100 c. c. of hot and 25 c. c. of cold water ; the last washing required three-tenths of one c. c. of  $\frac{N}{10}$  NaOH for neutralization and the acidity of each successive wash varied irregularly. By the distillation process the condenser became almost clogged with the fatty acid that volatilized and condensed on its walls. This, of course, was reckoned as insoluble fatty acid. Owing to the fact that the washings in the wash process are filtered hot, while the distillate in the distillation process is filtered cold, the soluble acids in the first, in the case of an oil like cocoanut that contains a large proportion of fatty acids soluble with difficulty in water, are higher than in the latter process. In the analysis of butter and oleomargarine the writer has found the distillation process of great service and in every way reliable.

The results above given were all obtained by the writer in the laboratory of Dr. E. Waller, New York.



REGULAR MEETING, DECEMBER 6TH, 1889.

The annual meeting was held December 6th, 1889. President C. F. Chandler in the chair.

The minutes of the previous meeting were read and adopted.

The President, in making an informal report upon the condition of the society, expressed a hope of seeing greater progress made, and recommended that the changes in the Constitution already proposed, or to be proposed, be examined and so far carried through that a reorganization of the society might be made up on the plan of the Society of Chemical Industry.

Prof. Breneman reported, informally, from the Board of Directors.

The report of the Treasurer was read.

The committee appointed at the November meeting to canvas the society for papers, etc., reported through Messrs. Geisler and Doremus that they had secured a number of papers for the Journal and would continue their work.

The annual election being next in order, Messrs. Hallock and Wainwright were appointed Tellers. Messrs. Alsberg and Stebbins, who were elected Corresponding Secretary and Treasurer respectively, on this ballot, declined re-election. Their places were filled by the unanimous election, of A. C. Hale as Corresponding Secretary, and F. T. King as Treasurer.

The officers elected for the year 1890 are as follows :

President : H. B. Nason.

Vice-Presidents : C. E. Munroe, G. A. Koenig, A. B. Prescott, A. A. Breneman, C. F. Chandler, Elwyn Waller.

Corresponding Secretary : A. C. Hale.

Recording Secretary : C. F. McKenna.

Treasurer : F. T. King.

Librarian : William Rupp.

Curators : A. C. Hale, Frank Vanderpoel, C. E. Munsell.

Committee on Papers and Publications : J. F. Geisler, A. A. Breneman, A. C. Hale.



Committee on Nominations : Hermann Endemann, C. A. Doremus, T. S. Gladding, T. D. O'Connor, A. P. Hallock.

Board of Directors : A. A. Breneman, Elwyn Waller, C. F. Chandler, C. F. McKenna, A. C. Hale, T. D. O'Connor, J. H. Stebbins, Jr., W. Rupp, F. T. King, H. Endemann, W. H. Kent, L. H. Friedburg, J. F. Geisler.

Letters were read from Prof. C. E. Munroe on the subject of reorganization, also some amendments to the constitution proposed by the same gentleman, which were referred to the Board of Directors.

Prof. Breneman reported the results of a conference held with the Vice-Chancellor of the University, on the subject of library and meeting room facilities for the society.

Messrs. Breneman, Geisler and Rupp were appointed by the chair as a committee to conclude the arrangements, subject to the approval of the Board of Directors.

Mr. Munsell moved the appointment of an auditing committee to examine the accounts of the Treasurer for the year 1889. Messrs. Alsberg and Rupp were appointed.

The following nominations for membership were presented : Otto P. Amend, of New York ; August Seher, of Newark, N. J. ; Dr. Thos. B. Stillman, of Stevens Institute, Hoboken, N. J. ; Oscar Texter, Cleveland Rolling Mills, Cleveland, O. ; Lieut. Willoughby Walke, U. S. A., Instructor in Chemistry, Artillery School, Fortress Munroe ; Dr. Wm. L. Dudley, Prof. Chem., Vanderbilt University, Nashville, Tenn.

The resignation of Prof. F. P. Dunnington of the University of Virginia was read and accepted.

The paper of Mr. Rupp was read by title "Analyses of two Minerals."

Mr. Wainwright read by title a paper on "The Examination of Commercial Glycerine."

The meeting was then adjourned.

CHAS. F. McKENNA,  
Rec. Secretary.

## ANALYSIS OF MARINE OILS.

BY RUSSELL W. MOORE, A. M., M. SC.

In connection with an extended examination of a large number of oils and fats, the results obtained in the case of some porpoise and blackfish oils were of so unusual a character as to deserve particular mention.

It has for some time been considered that the analysis of the various fats and oils occurring in nature would show a percentage of insoluble fatty acids amounting to some figure in the neighborhood of 95 per cent. A notable exception is butter fat, in which the insoluble fatty acids range between 87.5 and 89.5% and, in some cases, even slightly higher. The first chemical process used to distinguish butter from other fats was based solely upon this difference. Later, cocoanut oil was found to contain fatty acids soluble in large amounts of water and sufficient washing was found to reduce the per cent. of insoluble fatty acids to a figure even lower than that given by butter (*Chem. News*, Dec. 5th, 1884).

It must, however, be granted that while this opinion was founded on a very large number of analyses of butter, the number of such analyses made on other fats was extremely small when the great number and variety of fats and oils occurring in nature is taken into consideration. Oleomargarine, beef and mutton suet and lard, and a few oils, comprised nearly the whole list of fats analyzed.

An examination, however, of most of the natural fats and oils serves to establish in most cases the fact that the insoluble fatty acids amount to about 95 per cent. A notable exception is found in the case of some marine oils examined by the writer.

The oils in question are known in the market as porpoise jaw and blackfish jaw oils, and are obtained from the soft fat of the head and jaw by allowing the oil to exude from the fat. The oil thus obtained is exposed to cold and the portion remaining fluid racked off. The resulting oil, carefully skimmed and strained, is of a straw yellow color, thin and limpid, and by no means of an un-

pleasant odor. It is used for lubricating fine machinery and commands a very high price.

The oils examined were five in number, as follows :

- No. 1. Porpoise jaw oil skimmed and strained.
- No. 2. Porpoise jaw oil skimmed and strained.
- No. 3. Porpoise jaw oil not skimmed and strained.
- No. 4. Blackfish jaw oil skimmed and strained.
- No. 5. Blackfish body oil.

The oils were first examined by the wash process to determine the percentages of soluble and insoluble fatty acids. The results were as follows, the figures given being the mean of duplicates agreeing closely.

	Soluble Fatty Acids.	Insoluble Fatty Acids.
No. 1.....	17.18%	72.05%
No. 2.....	21.44	68.41
No. 3.....	----	96.50%
No. 4.....	21.79	66.28
No. 5.....	2.46	93.07

The oils were next examined by the Reichert process with the modification suggested at the time by Dr. Waller. The distillation was continued by adding 50 c. c. of water to the flask and distilling until a practically neutral distillate was obtained adding 50 c. c. of water between distillations, titrating as in the Reichert process and calculating the acidity to butyric acid.

The results obtained were as follows :

	Reichert Figure.	Total Acidity.
No. 1.....	47.77 c. c.	17.18%
No. 2.....	56.00	20.97
No. 3.....	2.08	1.42
No. 4.....	65.92	24.31
No. 5.....	5.60	2.34

The saponification number was obtained by the process of Koettstorfer. Considerable difficulty was experienced in this determination in obtaining concordant results, since the combination of the alkali with the fat appeared so feeble that even very dilute standard hydrochloric acid appeared to decompose the soap and

liberate fatty acids. This was seen on diluting with water, when oily drops would appear while the liquid was still alkaline. By using large quantities of alcohol concordant results were obtained as follows :

	Mgs. K O H per Grm.
No. 1.....	253.7
No. 2.....	272.3
No. 3.....	143.9
No. 4.....	290.0
No. 5.....	197.3

The iodine coefficient was also determined by the Hübl method and gave the following results :

	Grms. Iodine per 100 Grms.
No. 1.....	49.6
No. 2.....	30.9
No. 3.....	76.8
No. 4.....	32.8
No. 5.....	99.5

It will thus be seen that the oils which had received the full treatment furnish abnormally high figures for soluble or volatile fatty acids and correspondingly low figures for the insoluble fatty acids. They constitute the most notable exception to ordinary fats in this respect. Of course the high per cent. of soluble acids is due to the treatment which the oils undergo in the refining process by which the glycerides of the lower fatty acids are concentrated in the oil that is finally strained off. This is conclusively shown by the foregoing figures, oils Numbers 1, 2 and 4, that received the full treatment, giving extraordinarily high results for soluble fatty acids and saponification equivalent and correspondingly lower iodine absorption coefficients, since the lower glycerides are of the acetic acid series and are indifferent to iodine.

The volatile acid present in these oils should be calculated to valeric acid. It was, however, calculated by butyric acid by the writer in order that the results should be comparable with other analyses.

It would be a matter of interest to conduct some experiments with butter fat by subjecting it to a similar process of freezing

and straining and examining the resulting product, and the writer proposes to conduct such a series at his earliest opportunity. Valuable information regarding the nature of the composition of the molecular groupings in butter fat in this way may be obtained.

The oils examined as above were obtained by Dr. E. Waller from the manufacturer and the analyses were made in his laboratory, New York City, and under his direction.

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The Journal

—OF THE—

AMERICAN CHEMICAL SOCIETY.

VOLUME XII.  
1890.

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NEW YORK:  
JOHN POLHEMUS,  
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1890.



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C. F. MCKENNA,  
Recording Secretary

\* The first two papers on the list will be found in the two preceding numbers of the Journal November and December, 1899, respectively; they were published in advance of date because of previous delay in the issue of the Journal. — Ed.



[illegible]

**JAMES H. STEBBINS, JR., Treas.**

## ANNOUNCEMENT.

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### REVISION OF THE CONSTITUTION.

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The Committee on Revision of the Constitution and By-laws of the American Chemical Society, appointed by the Board of Directors at the meeting held Jan. 7, 1890, ask the co-operation and assistance of members of the Society, and other chemists, in their work.

It is desired that the revised Constitution may be free from the objections that have been urged against the present Constitution, and that it may be the basis of a more general organization of American Chemists.

Suggestions as to changes in the present Constitution, or introduction of new sections, will be carefully considered by the Committee. It is expected that the report of the Committee will be ready for action by the Board of Directors by March 5th, and a printed copy of the revised Constitution will then be presented to every member of the Society to be voted upon.

Communications should be forwarded as soon as possible.

A copy of the present Constitution is mailed to each member with the present number of the JOURNAL.

All communications should be addressed to J. H. Stebbins, Jr.  
114 Pearl street, New York.

Very respectfully,

J. H. STEBBINS, JR.,	} Committee.
L. H. FRIEDBURG,	
J. F. GEISLER,	

## EDITORIAL.

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The prospects of the American Chemical Society for the year 1890 seem brighter than for several years past, and there is reason to hope that the present number of the Journal may be the beginning of a volume that shall more worthily represent the original aims and purposes of the Society. The Journal must be, in any case, the measure and indicator of the scientific vigor of the Society; its function is primarily to chronicle the acts and doings of the Society; and without some basis of scientific work accomplished and to be reported, the journal of the Society has no *raison d'être*. Abstracted and selected matter have a certain place in it, but not the first place. It would be easy to make of the journal a mere eclectic, bearing the name of a torpid organization and drawing its sustenance from the work of other societies, but this would not be fulfilling its purpose. How fully its proper function has been filled during the past four years it is not necessary to say. To say that it and the society which it represents have been kept alive mainly by local effort during that period is, perhaps, a doubtful comment upon the propriety of the existence of either, and the fact is only to be justified by the faith of those who believe that it is worth while to maintain the form and charter of an established national organization until events will enable it to make good its original purpose. The Journal has to thank its friends for such support as has been given it and to ask the renewed interest of those who have had only criticism to give where it might justly have expected coöperation.

The meeting of November 1st, 1889, was made the occasion of a general discussion of the affairs of the Society. The attendance was exceptionally large and the practical result of the meeting was the appointment of a committee to secure pledges of money and scientific material to permit of the regular issue of the journal. The improvement in the outlook of the Society for the present year is largely due to the work of this committee. A large number

#### EDITORIAL.

of papers have been promised by members and the treasury has been replenished to such an extent that the dues of members for the year 1890, together with the funds now in hand, will amply provide for the expenses of the journal.

Apart from this, negotiations which have been in progress for some time have resulted in securing free rooms for the meetings of the Society and storage for its books, journals, etc., in the building of the University of the City of New York. The library will be placed, as a separate collection, in the library of the University, accessible at all times and under the eye of the librarian, who is always present. For working purposes the library will be more available under the new arrangement than it has been heretofore.

The revision of the Constitution of the Society has been under discussion for several months, and a committee has recently been appointed by the Board of Directors to prepare a report upon this subject. An announcement of this committee will be found in the present number of the journal. It is desirable that this revision should be thorough and that the new Constitution may be the basis of a reorganization of the Society that may enable it to meet more fully the needs of a national organization of chemists.

This brings us to the question which has been much under discussion during the past two years, namely, the best method of securing more thorough organization and coöperation among chemists in America.

The proposal to organize upon the basis of the American Chemical Society, while providing for local sections and for an annual meeting with the American Association for the Advancement of Science, has been debated and is still under discussion; undoubtedly it contains the true elements of the solution. The writer, however, speaking only for himself, would question the desirability of fixing the place of meeting at present. It would seem better to leave the decision to the Society at its annual meeting. The annual meetings should be held in different places successively in order to appeal more fully to that local feeling which is an element always to be considered; but it may well be ques-

tioned whether a constitutional provision linking the Society so closely to the American Association is desirable. The writer takes the liberty of modifying, somewhat, his views upon this question as expressed when the question was first broached. The matter has been under discussion at two successive meetings of the American Association and has failed there to secure decided support. Moreover, the number of chemists in attendance at these meetings has not been large enough of late to accurately represent the sentiment of the chemists throughout the country.

The time of the Association meeting, midsummer, is no more suitable, on the whole, for the majority of chemists than the Christmas holiday season would be, and an annual meeting in one of the large cities at that time would probably be an occasion of more interest and better work than one held in Summer. The experience and usage of such bodies as the National Academy and the Society of Mining Engineers are worthy of consideration upon this point. As the Chemical Society could probably have only one general meeting each year at first, it should give even more attention to the question of time and place than these societies, while adhering, like them, to the peripatetic principle.

As to the question of local *habitat* for a national society the writer believes that a place of deposit for books and papers, a meeting room and library and a place of general rendezvous would add to the dignity and efficiency of the organization. Such a place can only be found in one of the large cities, and New York, as the most populous centre and the gathering point of more than two hundred chemists, has the best claim to it. But, whatever may be the issue of the present discussion, the American Chemical Society may be counted upon to act in accordance with the best interests of chemistry and with the general opinion of American chemists, whenever a clear expression of such opinion can be obtained. In undertaking a radical revision of her constitution and asking the assistance of all chemists in the work, the Society is taking the course which, in the opinion of its members, will lead most directly to the solution of the whole question.

ON THE ACTION OF NITROUS ANHYDRIDE (NITROGEN  
TRIOXIDE), DISSOLVED IN CARBON DISULPHIDE,  
UPON DIFFERENT ORGANIC COMPOUNDS.

BY L. H. FRIEDBURG AND JOHN A. MANDEL.

(*First Paper.*)

The action of free nitrous anhydride upon organic bodies capable of reacting with it, varies greatly and is generally productive of changes more profound than simple substitution. But if under the influence of this action substitution products are formed, these belong to the nitroso, or to the isonitroso, compounds. The formation of nitro products, however, in this manner is exceptional.

Thus, primary amines of the fatty series are changed into the corresponding hydroxyl derivatives, while secondary amines yield nitroso amines and tertiary amines are not acted upon. Amido bodies of the aromatic series are transformed into diazo compounds, while the imide group gives rise to nitroso derivatives.

Some investigators have found the action of nitrous anhydride to be oxydizing\* upon hydrocarbons and substituting in the highest degree upon phenol† forming picric acid with the latter. An easily accessible reference for the general literature of this action of nitrous anhydride upon organic bodies is Beilstein's Handbuch der Organischen Chemie, 1886. (Vol. I., pp. 110 and 111.)

It has seemed to us that in lessening the violence of this reaction by the diluting influence of some third substance of indifferent behavior new results might be obtained. Other chemists have attempted in a general way to control the method and make it more readily available. Thus Stenhouse & Groves‡ used a solution of nitrous anhydride in conc. sulphuric acid to prepare nitrosophenol and Weselsky§ used common ether as a diluent

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\* A. R. Leeds, J. Am. Chem. Soc., 2 (1880), 17.

† A. R. Leeds, J. Am. Chem. Soc., 2 (1880), 422.

‡ Ann. Chem. (Liebig), 188, 354.

§ Ber. chem. Ges., 8, 98.

for  $N_2O_3$  in the preparation of diazophenol nitrate and mononitro phenols. About fifteen years ago, one of us, experimenting then on carbon disulphide, found this latter to be an excellent solvent for gases of very different character, and at that time \* tried the action of nitrogen dioxide dissolved in  $CS_2$  upon different bodies. The results not being of special interest, although they showed the possibility of obtaining substitution as well as addition products† in this way, the use of a solution of nitrous anhydride in carbon disulphide suggested itself as the next step. The results here submitted are to be regarded as preliminary only; the authors intend to pursue the investigation and to apply the reaction above mentioned in many different cases.

First as to the preparation of nitrous anhydride. Arsenious oxide ( $As_2O_3$ ) in very fine powder is treated with c. p. nitric acid of 1.42 sp. gr. in a capacious flask provided with delivery tube and thistle tube with safety bulbs. The gas is slowly generated and passed through several U tubes filled with spirals and flat pieces of test lead so as to free the gas from all nitric acid. The receiver, from the start, is surrounded with a mixture of ice and salt, and the green liquid obtained is redistilled once from this receiver into a similar one which is put into the freezing mixture while the first is immersed in tepid water. Thus a clear, dark blue fluid is obtained and only traces of liquid nitric acid remain in the original receiver.

The  $N_2O_3$  thus prepared is then gently poured into carbon disulphide, previously purified and freed from dissolved sulphur, by shaking it at intervals, for a day or more, with mercury. The mixture of  $CS_2$  and  $N_2O_3$  must also stand in the freezing mixture. This is the nitrous anhydride solution as we invariably use it. The body to be acted upon is likewise dissolved in  $CS_2$  and kept in the cooling mixture. The nitrous anhydride solution is added to the solution to be treated very slowly, best in drops. The heat of the reaction is thus kept down as much as possible and the spontaneous evaporation of some of the  $CS_2$  assists in the reduction of temperature. The organic substances which have thus

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\* Ber. d. chem. Ges., 8, 1616.

† J. Am. Chem. Soc., 4, 252, 1882.

far been submitted to the action of nitrous anhydride by the above methods are benzol, phenol and diphenylamine.

*Benzol and Nitrous Anhydride.*—The products under these conditions are exclusively mono-nitrobenzol and para-dinitrobenzol; the latter, which is formed in larger quantity, occurs in flat crystals, which after the first recrystallization melt at exactly 89° C. Under the conditions it could not be ascertained whether nitrous oxide was amongst the products of reaction; but if this be assumed, as it may be, according to the investigations of Leeds\*, we may write as the equation for this reaction:

$C_6H_6 + 2N_2O_3 = \text{para } C_6H_4(NO_2)_2 + H_2O + N_2O$ , while for the formation of mononitrobenzol, which is obtained at the same time, the equation would be:

$2C_6H_6 + 2N_2O_3 = 2C_6H_5NO_2 + H_2O + N_2O$ . According to this equation two molecules of benzol must take part in the reaction, and, since an excess of nitrous anhydride was used, the predominance of the dinitro compound is explained.

Leeds (*loc. cit.*) working with undiluted nitrous anhydride obtained, in addition to mononitrobenzol, oxalic acid *with water of crystallization*, and the formation of this latter makes it more than likely that our reactions took place in the manner above suggested.

*Phenol and Nitrous Anhydride.*—In this case the results corresponded in part to those of Weselsky (*loc. cit.*) who used common ether as a diluting agent and obtained orthomono- and paramono-nitrophenol, but Weselsky obtained at the same time diazophenol nitrate, which precipitated; of this we did not obtain a trace, while nitrosophenol formed one third of the products in our experiment. Very small quantities of higher nitro compounds, which formed also, may, for the present, be neglected.

The greater part of the volatile orthonitrophenol remains dissolved in the carbon disulphide, while none of the paranitrophenol is dissolved. This solution is easily decanted from the underlying liquid which contains some ortho, and all of the para and nitroso compounds. The separation is effected by distillation in a

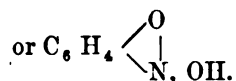
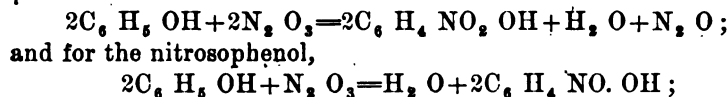
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\* J. Am. Chem. Soc. 2 (1880), 426.



current of steam and the para compound is thus left in the retort, but portions of it, though not volatile, as well as some of the non-volatile nitroso compound are carried over into the distillate, which renders purification necessary. The distillate is shaken with ether. From this solution, which was not yellow but strongly dichroic between purple and green, olive green crystals of orthonitrophenol were obtained. These, when redissolved in water and distilled in a small fraction tube at gentle heat, yielded a crop of beautiful, straw yellow crystals of orthonitrophenol which melted at 45° C.

The remaining liquid in the fraction tube showed Liebermann's nitroso reaction and decomposed to black, powdery bodies as impure nitrosophenol does. The paranitrophenol was crystallized from its solution and, after frequent recrystallizations, was obtained in crystals an inch in length, showing the exact melting point of 114° C. The reaction offers us also two well defined equations. For the formation of the two isomeric mononitrophenols:



*Diphenylamine and Nitrous Anhydride.*—This reaction was effected in three different ways:

I.—The diphenylamine was dissolved in absolute alcohol and the solution of nitrous anhydride in  $\text{CS}_2$  was added. The alcohol not having been sufficient to keep all the carbon disulphide dissolved, enough was added to obtain a uniform solution.

II.—The diphenylamine as well as the nitrous anhydride were separately dissolved in  $\text{CS}_2$  and the solutions were then mixed.

III.—Experiment II. was repeated with diphenylamine dissolved in  $\text{CS}_2$  in which an equivalent amount of sulphur had previously been dissolved.

I. This experiment furnished after twelve hours an abundant quantity of light wax yellow needles a quarter of an inch long,

which had in crystallizing adhered to another compound forming small, brick-red, warty masses. The separation of these two compounds was based upon the lesser solubility of the red portions in ether and their greater solubility in benzol. Very small quantities of ether were added to the bulk of the mixture of crystals after they had been very thoroughly pressed between filter paper. Thus solutions were obtained which on crystallizing gave an abundance of the yellow and but few of the red crystals. Repeated, insufficient exhaustion of these with ether, gave us finally, perfectly pure, light amber colored, thick prisms, which were paramononitrodiphenylamine, melting at 133° C.

The red portions, also crystallized from ether (benzol was abandoned as a solvent, because the substance, as long as it was not quite pure, separated too slowly from this solvent) were subjected to sublimation and yielded a beautiful, scarlet red sublimate of very long needles, melting at 210° C., thus indicating that the compound was orthodinitrodiphenylamine. In one particular portion of the ethereal solution of the *para* compound, a large quantity of thick, hard, garnet-red crystals which appeared to be rhombic octahedra were obtained. Crushed in a mortar these crystals gave an orange-yellow powder, melting at 215° C., properties characteristic of paradinitrodiphenylamine.

II. and III. The carbon disulphide solution of diphenylamine, to which equivalent amounts of sulphur had been added, when mixed with solution of  $N_2O_3$  in  $CS_2$ , yielded, on rapid evaporation, principally crystals of paramononitrodiphenylamine, melting at 133° C. When, before evaporation, absolute alcohol was added, the total amount of sulphur was precipitated. The sulphur had been added in order to see whether this element, which reacts so easily with diphenylamine, could not, simultaneously with the nitro-group, be incorporated into it.

In experiment I, the mother liquors were allowed to crystallize to the very last drop and thus, successively, mixtures of crystals were obtained which appeared progressively darker. The formation of nitroso compounds was suggested by the dark greenish coloration and the perceptibly acid odor of the latter portions.

We have made a number of varied qualitative experiments upon

other compounds of the aromatic series and intend soon to describe the action of  $N_2O_5$  in  $CS_2$  solution upon the aldehydes, acids and amido derivatives of the same.

*College of the City of New York, January 3d, 1890.*

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## ON THE ALLEGED STERILIZATION OF RIVER WATER BY MINE WATER.

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BY A. A. BRENNEMAN.

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During an epidemic of typhoid fever which occurred in the city of Wilkesbarre, Pa., in the Summer of 1889, questions arose as to the purity of the different sources of water supply upon which the city depended, and the writer was called upon to make an examination of the waters in question. The water of the Susquehanna River is one of these and is the only one concerned in the present discussion. The history of the epidemic and its causes is not at present to the purpose.

It was found that the river water was preferred by the public and by local physicians to water from adjacent mountain streams in spite of the fact that it receives above Wilkesbarre the sewage of nearly 100,000 people in the course of ten miles, the city of Scranton, which discharges its sewage into the Susquehanna through a tributary, the Lackawanna, and of Pittston, which is directly on the river, being the principal sources of contamination.

This peculiar faith in the purity of a river so open to defilement is traceable in part to the general indifference to filth that is known to be largely diluted, but much more to the influence of certain articles published in the local papers with the stamp of official commendation and the authority of scientific or *quasi* scientific opinion.

It was believed by the people of Wilkesbarre that the river water was peculiarly free from possibility of transmitting infectious diseases because of the considerable quantities of mine water

which it receives, the mine water being supposed to exert a sterilizing effect through its well known constituents, free sulphuric acid and sulphates of iron.

As it seemed that this belief, which was supposed to rest upon a scientific basis, could best be upset by direct scientific tests, the writer proceeded to make the following examinations :

Samples of water were taken,

1. From the Susquehanna River at the intake of the Wilkesbarre Water Co.
2. From the mouth of the shaft of the Hollenbach coal mine, the drainage from which runs into the river above Wilkesbarre.
3. (For comparison only) From Mine No. 3 of A. Pardee & Co. (coal operators at Hazleton, Pa.), at a depth of 300 feet from the surface.

The above samples were examined chemically and biologically with the results given below.

#### CHEMICAL EXAMINATION.

	GRAINS PER U. S. GALLON.					
	Total Acid (SO <sub>3</sub> ).	Free Sulphuric Acid H <sub>2</sub> SO <sub>4</sub> .	Ferric Oxide, Fe <sub>2</sub> O <sub>3</sub> .	Lime.	Magnesia.	Silica.
River.....	1.00	.00	.71	1.88*	.46†	.....
Hol. Mine....	51.16	15.59	12.23	8.21	4.09	2.50
Haz. Mine....	127.30	20.85	65.40	2.55	4.27	2.70

The iron present in the mine waters was entirely peroxidized when received, and as it was contained in well corked bottles with very small vacant spaces above the liquid it had probably had little chance to change after bottling.

The river water was alkaline in reaction and contained no iron in solution; the portion present being suspended ferric oxide.

These qualitative data alone dispel the idea that the river water can retain at Wilkesbarre any of the germicidal power that may be possible to salts of iron or free sulphuric acid.

\* Equivalent to 2.1 grains calcium carbonate or 1.7 grains calcium sulphate.

† Equivalent to 0.96 grains magnesium carbonate.

The mine waters are quite acid and the quantity of free acid irrespective of the ferric sulphate in solution (calculated from the ferric oxide present, although a portion of this had been precipitated when received), was sufficient to permit of some germicidal effect.

As the total sulphuric acid in the river water (all of which is combined) is only one grain per gallon, it is not possible to admit that any quantity of this acid that is relatively important can reach the river throughout its entire course of more than a hundred miles above Wilkesbarre, and as all of this acid, which has once entered the river, must remain in the water as soluble sulphates the inflow of the mine water must be quantitatively insignificant.

*Bacteriological Examinations.*

In view of the important part played by bacteriological evidence in such discussions as this, it seemed well to examine the above waters also for bacteria, and as a crucial test, to attempt the cultivation of the specific bacillus of typhoid fever in the water of the river after it had been sterilized by heat.

To this end new samples of the waters 1 and 2 were taken in sterilized bottles, with the necessary precautions, and submitted to Dr. Hermann Biggs, of Bellevue College Hospital, a well known specialist in bacteriology, for the necessary bacteriological examination.

The results of Dr. Biggs' examination showed that the sample of river water contained from 400 to 500 germs per c. c. of at least fourteen different species, six of these being of species that signify gelatine (putrefactive bacteria). When samples of this water was sterilized by discontinuous heating, inoculated with pure cultures of typhoid bacillus, allowed to stand for forty hours and then put into an incubator, the typhoid bacillus was found to be active at the end of forty-eight hours and apparently to have increased in numbers. The sole purpose of this experiment was to demonstrate, that there is not present in the river water any inorganic substance that can exert an inhibitive action upon the life or growth of the typhoid bacillus.

Further experiments showed also that the mine waters contained yeast and mould fungi, but no bacteria, although bacteria could

be developed in both by inoculation with appropriate cultures after sterilization, provided a small quantity of nutritive gelatine were added. As to the typhoid bacillus it was found that its growth (after treatment as in the case of mine water alone) was possible in No. 2. (Hollenbach mine water) but not in No. 3. As the proportion of free sulphuric acid is very slightly higher in No. 3 than in No. 2, the difference must apparently be ascribed to the much larger proportion of ferric salts in the Hazleton mine water.

In conclusion, it is evident that no effective sterilization of the water of any large stream can result from the small and varying contributions made to its volume by mine drainage since surface waters are certain to overpower any specific effect which the former might be capable of exerting, and the results of the foregoing examination render it unlikely that even mine waters of such strength as are commonly met with could, even undiluted, be of certain effect with germs having the high resisting power that the typhoid bacillus is known to possess.

It is certain, moreover, that a water rich enough in sulphuric acid or iron salts to act as a disinfectant would be entirely unsuited for drinking.

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## ABSTRACTS.

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### GENERAL CHEMISTRY.

**Analysis of the Seed of *Calycanthus Glauca*. H. M. WILEY.\***

The above plant is a shrub growing in the mountains of the Southern States from North Carolina to Georgia. The berries, known locally as "bubby" berries, are violently poisonous, and

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\* See also a paper by L. E. Sterns on the Fruit of the *Calycanthus* (Bulletin of the Torrey Botanical Club, August, 1888,) and by R. G. Eccles, in *Western Druggist*, Jan., 1889, p. 15, and in *Druggists' Circular*, March 1889, p. 65.

being rich in sugar are apt to be eaten by cattle, and many cases of poisoning have resulted. The author has determined the composition of pod, hull and kernel of the fruit. The seed is very rich in oil, containing about 50 per cent. The oil is faint yellow of Sp. Gr. 9058 (extracted by solvents) to .9110 (expressed), contains no volatile acids, yields a fatty acid crystallizing at  $12.5^{\circ}$  and, judging by its iodine coefficient, the oil has moderate drying properties, which, however, were not further determined. The oil also contains a trace of the peculiar alkaloid "Calycanthine," which exists in the kernels in the proportion of 1.96 to 4.25 per cent. of the oil-free, dried kernels, the proportion depending upon the method of extraction. The hulls also contain the alkaloid to the extent of .83 per cent. Calycanthine yields the following colors with reagents :

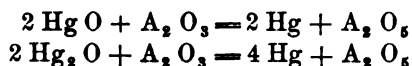
$H_2SO_4$ , pale yellow ;  $HNO_3$ , bright green (persistent) ;  $H_2SO_4$  and cane sugar, fine purple (persistent, but changing finally to blue) ;  $H_2SO_4$  and  $K_2CrO_4$ , fine blood brick red. Analysis of calycanthine leads to the formula  $C_{18}H_{40}O_{11}N_4$ . (*Am. Chem. Jour.*, 11, 1889, No. 7.)  
A. A. B.

#### **Influence of Food and Animal Idiosyncrasy on the Composition of Butter.** H. W. WILEY.

An investigation of some peculiarities in composition of butter fat first noted at the Agricultural Experiment Station of Texas where the cattle were fed upon cotton seed meal. The volatile acids in such butter were found to be abnormally low, reaching 21.00 as compared with 28.50 for butter from cows fed on other feed. The cotton seed butter had the phenomenally high melting point of  $45^{\circ}C.$ , yielded the iodine number 33.40, and exhibited strong reducing properties with silver nitrate. Experiments made with cows fed largely on cotton seed meal after feeding for a time on grass confirmed the above results only in the main. The experiments indicated, however, that cows fed only upon grass may yield butter so low in volatile acids, in exceptional cases, as to cast doubt upon the validity of the Reichert process, taken alone, as a means of deciding upon the character of butter. (*From a paper read before the Society for the Promotion of Agricultural Science, Toronto Meeting, Aug., 1889.*)  
A. A. B.

**Determination of Mercury. W. FEIT.**

In alkaline solutions of mercury compounds arsenious acid precipitates metallic mercury on boiling, according to the equations :

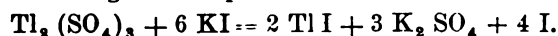


Upon these reactions the author bases the following method. If mixtures of mercurous and mercuric compounds are under examination, oxidize to mercuric salt by boiling with nitric acid. The removal of the latter is not necessary as it does not interfere in the final titration.

To the solution of the mercury salt add an excess of NaOH solution, and an excess of  $\frac{2}{10}$  arsenious acid. Boil the liquid for 10–15 minutes, cool, dilute to definite volume, filter and take an aliquot part for titration with  $\frac{2}{10}$  iodine solution. Neutralize the aliquot part taken with HCl and make alkaline by addition of NaHCO<sub>3</sub>, then titrate, using starch paste as an indicator. The quantity of arsenious acid actually required indicates the amount of mercury. (*Ztschr. anal. Chem.*, 28, pp. 318–322.) J. F. G.

**Determination of Thallium. W. FEIT.**

The author proposes a quick volumetric method depending upon the reaction between thallic salts and potassium iodide, in which the amount of liberated iodine indicates the quantity of thallium present, according to the equation :



It is essential that the thallium be present as thallic salt, preferably thallic sulphate, to effect which add to the thallium compound an excess of sulphuric acid, boil the solution and oxidize the same by adding bromine water. Continue the boiling to expel the excess of bromine. To the thallic solution thus obtained add an excess of KI, neutralize the free acid by adding an excess of NaHCO<sub>3</sub>, then add an excess of  $\frac{2}{10}$  arsenious acid solution. Allow the solution to stand for some minutes after repeated shaking until the precipitate has a pure yellow color. If the operation is performed in a graduated flask, fill up to the mark, allow the



precipitate to settle, decant or filter and take an aliquot part for titration with  $\frac{N}{10}$  iodine solution from which calculate the amount of arsenious acid actually required for the free iodine of the first operation, which indicates the quantity of thallium present. In some cases thiosulphate may be used in place of the arsenious acid solution. (*Ztschr. anal. Chem.*, 28, 314-316.) J. F. G.

**Incineration of Sugars and of Sirups without Sulphuric Acid.** JEAN LUCIEN.

The author admits the utility of the method of incinerating sugars and syrups in a current of pure oxygen gas, but maintains that it is industrially impracticable when a large number of determinations have to be made in a comparatively short time. He has obtained absolutely concordant results in less time than when operating with the aid of sulphuric acid, by mixing with five grammes of sugar or three grammes of syrup, one per cent. of zinc oxide in the former case or two per cent. in the latter, and incinerating the mixture in a platinum capsule over a Bunsen's gas jet; subsequently calcining at the entrance of a muffle heated to dull redness. (*La Sucrené Indigène et Coloniale*, from "*Bulletin de l'Association des Chimistes*," March, 1889.)

F. T. K.

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**Abstracts of American Patents Relating to Chemistry.**

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(From the U. S. Patent Office Gazette.)

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(Issued January 7th, 1890.)

**418,675.**—Direct-pointed adhesive negative. J. Baynes.

**418,711.**—Process of manufacturing gas. A. O. Granger.

The process consists in raising a body of carbonaceous material to a high degree of heat by burning it with air, and at the same time burning the gaseous products of combustion with air and highly heating a body of refractory material, then suspending the combustion and introducing directly into the coolest portion of the heated refractory material hydrocarbon liquid, causing it to pass through the refractory material in a direction the reverse of that in which the products of combustion passed through during the process of heating, then at the same time causing

steam to pass through the highly heated carbonaceous material and be decomposed into carbon monoxide and hydrogen, then causing such gas, as fast as it is generated, to pass through the refractory material in the same direction and in company with the hydrocarbon liquid, and thereby combine with the vapors and gases of the hydrocarbon as they are generated by contact of the oil with the refractory material at successively increasing temperatures.

**418,719.**—Filter or strainer. W. A. Hepburn.

**418,761.**—Apparatus for making salt. F. Siedentopf.

**418,792.**—Process of aging liquors. J. A. H. Hasbrouck.

The liquor is confined in a vessel lined with carbon, and subjected to the action of heat and oxygen while in a fine state of division.

**418,801.**—Apparatus for dyeing. J. H. Lorimer.

**418,807.**—Gas blowpipe. D. M. Monroe.

**418,814.**—Pharaoh's Serpent. C. Nelson.

**418,864.**—Apparatus for the production of oxygen. L. Chapman.

**418,872.**—Process of Pasteurization of beer. W. Kuhn.

**418,916.**—Blue dye. B. Homolka.

A blue violet coloring matter, formed from aniline, aniline hydrochloride and amido azo benzol. The formula is  $C_{14}H_{18}N_4$ .

**418,947.**—Crayon. A. Hart.

Consists of a pigment and carnauba wax, stearic acid and paraffin.

**419,023.**—Filter. C. V. Roberts.

**419,098.**—Apparatus for making oil gas. T. Alexander and S. Alexander.

**419,106.**—Paint composition. J. Bollinger.

Consists of ammonium chloride, quick lime, boiled oil, salt and water.

**419,168.**—Black pigment. A. G. Wass.

Consists of calcareous earthy substances, as chalk, impregnated with saccharine matter, and particularly the earthy refuse of sugar refineries, calcined or burned.

*(Issued January 14th, 1890.)*

**419,195.**—Process of separating solder from tinned iron. W. E. Harris.

The tinned iron is coated with petroleum, and the latter burned on the iron to melt off the solder, in a suitable receptacle.

**419,215.**—Apparatus for producing fresh water from sea water. W. F. Pamphlett.

**419,224.**—Extracting apparatus. T. Scully.

**419,266.**—Filter. E. M. Knight.

Consists of asbestos cloth or other fibrous material and an exterior coating of a filtering medium in the form of paste spread upon the cloth and an exterior cover of wire screen to uphold the medium.

**419,274.**—Process of manufacturing iron and steel alloys. H. Marbeau.  
A malleable alloy, composed of iron or steel and nickel, the proportion of nickel being less than 25 per cent. of the whole, with manganese and aluminium.

**419,331.**—Process of scouring or dyeing. S. Hodgson.

**419,332.**—Alcoholic distillation. W. L. Horne.

**419,347.**—Process of purifying and deodorizing petroleum. R. M. Perrine.

The process consists in first agitating the petroleum with bleaching powder for five hours, more or less, then adding sulphuric acid to complete the elimination of the chlorine gas, and to neutralize and precipitate the alkaline matters and other impurities, and finally drawing off the purified and deodorized oil.

**419,350.**—Apparatus for washing gases. M. A. Piedra.

**419,404.**—Process of manufacturing basic linings for converters. E. Bestrand.

**419,533.**—Stove polish. A. J. Miller.

Consists of alkali soap, water, plumbago, and oil of bitter almonds.

**419,582.**—Solution for preserving wood. J. P. Card.

Consists of 979 parts water, 20 parts zinc chloride, and 1 part mercuric chloride.

**419,610.** Process of recovering salt and crude glycerine from spent lye. E. K. Mitting.

The process consists in adding lime to the lye, removing the precipitate thus formed, concentrating the lye until it is saturated or nearly saturated with salt, then again treating with lime and again removing the precipitate, then boiling down the lye without further treatment to the finishing point, removing the salt thus produced either during or at the end of the operation, and finally purifying the salt by washing with a solution of common salt which has been rendered alkaline by the addition of a small percentage of caustic or carbonated alkali.

*(Issued January 21st, 1890.)*

**419,655.**—Manufacture of artificial stone. J. F. Gesner.

**419,657.**—Artificial solid material. J. F. Gesner.

**419,671.**—Foam for carbonated beverages. G. C. Henry.

Consists of infusion or tincture of sarsaparilla, etc., solution of gelatin, syrup, and water.

**419,697.**—Process of reclaiming rubber from waste rubber goods. N. C. Mitchell.

The process consists in grinding the stock into small fragments, attacking and disintegrating the fiber, removing the mud and similar impurities by washing in water, separating the heavier foreign substances by flooding in water, and floating the rubber away from such heavy substances by

the action of a current of water, devulcanizing by the action of live steam under pressure and disintegrating the devulcanizing mass.

**419,707.**—Preparation of malt. G. Reininghaus.

**419,726.**—Neutralizing sulphochlorinated organic compounds. A. Sommer.

Sulphochlorinated organic compounds containing hydrochloric acid, are neutralized by digesting the compounds with a volatile unsaturated hydrocarbon.

**419,775.**—Construction of filter presses. S. H. Johnson and C. C. Hutchinson.

**419,779.**—Process of treating glue and gelatin moulds. G. Koller.

The glue or gelatine is dissolved in an aqueous solution of an energetic oxidizing agent, then formed in molds and finally exposed to the action of light.

**419,858.**—Process of preserving wood. C. T. Lee.

The wood is immersed in a solution of resinate of glycerin and naphtha and then subjected to heat.

**419,866.**—Fuel block. A. K. Murray.

Consists of saw dust, a binder of clay and water, and a hardening mixture of plaster of Paris and water.

**419,867.**—Fuel composition. A. K. Murray.

Consists of about seven parts lignite and about one part coal dust, with sufficient clay and water to bring the mass to the consistency of soft putty.

**419,868.**—Fire kindler. A. K. Murray.

Consists of fibrous material, such as: waste paper, straw, shavings, sawdust, spent tan bark, etc., treated with a mixture clay, water, and salt-peter.

**419,869.**—Artificial fuel. A. K. Murray.

Consists of anthracite and bituminous coal dust, and sawdust, with a mixture of clay and water.

**419,981.**—Process of distilling mineral oils and like products. James Dewar.

*Issued January 28th, 1890.*

**420,080.**—Process of treating silver and zinc ores. F. L. Bartlett.

The process consists in mixing the ore with hydrocarbon fuel, supplying sufficient sulphur to produce an excess of the same, burning in the presence of an air blast forced uniformly up through the whole mass of ore and supplying air to unite with the products of combustion above said mass.

**420,082.**—Composition for paint. J. P. Moser.

Consists of tar, ammonium carbonate, lamp black, whiting, copal varnish, Japan drier, coal oil and tincture of ferric chloride.

**420,180.**—Flexible photographic film. W. H. Walker and George Eastman.

**420,164.**—Blue dye. J. Mohler.

**420,311.**—Nitroso dye. A. F. Poirriere.

Obtained by heating in a suitable medium, such as water, a salt of a nitroso derivative of a secondary or tertiary amine and separating the coloring matter from the solution by precipitation with a mineral salt.

**420,315.**—Process of cleaning wool. K. F. Stahl.

Woolen fibers are recovered from rags containing woolen and vegetable fibers by treating them with a heated solution of oxidized pickling liquor, unoxidized pickling liquor, brine and sulphuric or hydrochloric acid.

**420,326.**—Artificial stone composition. A. M. Blackmon.

Consists of salt, sand, alum, Portland cement, plaster of Paris, zinc chloride and boiled linseed oil.

**420,371.**—Method of burning cement making materials. J. M. Wilcox.

**420,372.**—Blue dye. O. M. Witt.

Is prepared by combining 1 molecule of the (so-called "Broenner's") betanaphthylamine,  $\beta$ -sulphonic acid with 1 molecule of  $\beta$ -naphthohydroquinone. The composition corresponds to the formula  $C_{10}H_7(SO_3Na)-N=N-C_{10}H_6(OH)_2$ .

**420,373.**—Ammonium salt of  $\beta$ -naphthohydroquinone  $\beta$ -sulphonic acid.

O. N. Witt.

Produced by submitting amido-naphthol- $\beta$ -sulphonic acid to the successive action of oxidizing and reducing agents.

**420,374.**—Dark blue dye. O. N. Witt.

Results from the combination of 1 molecule of the so-called "Dahl's"  $\alpha$ -naphthylaminedisulphonic acid with one molecule of  $\beta$ -naphthohydroquinone- $\beta$ -sulphonic acid. The composition corresponds to the formula:  $C_{10}H_7(SO_3Na)-N=N-C_{10}H_6(OH)_2$ .

**420,394.**—Process of making ozone water. C. F. W. Stelzer.

Hydrochloric acid or hydrochloric acid and a chloride in small quantity is added to ozone water to preserve its properties.

(Issued February 4th, 1890.)

**420,428.**—Process of filtering oil. C. F. Baker.

**420,445.**—Soluble nitrocellulose and process of manufacture. J. R. France.

Cotton is mechanically reduced to a uniform and homogeneous dust-like mass and subjected to the action of a bath of nitric and sulphuric acids.

**420,446.**—Insoluble nitrocellulose and preparing the same. J. R. France.

Cotton in a dust-like condition is subjected to the action of a bath of

nitric and sulphuric acids in the usual proportions and strength at a temperature of about 24° for about 15 minutes.

**420,488.**—Process of making soda alum. E. Augé.

A solution of sodium sulphate and aluminium sulphate is evaporated in vacuo at a temperature not exceeding 60°, and then cooled and crystallized.

**420,515.**—Apparatus for washing rubber stock. N. C. Mitchell and S. P. Sharples.

**420,539.**—Carbonizing steel. Charles Jones.

Ordinary steel is dipped into oil or grease, then into soot, and exposed to heat in contact with powdered carbon.

**420,590.**—Vulcanizer. C. A. Davis.

**420,591.**—Carbureter. W. Dawson.

**420,598.**—Alloy. E. Golay.

Consists of about 40 parts platinum, 35 parts copper, and 25 parts nickel.

**420,615.**—Compound for parchmentizing paper. Emery Andrews.

Consists of dilute sulphuric acid, hydrochloric acid, zinc and dextrin.

**420,626.**—Dynamite. Egbert Judson.

Consists of a base of nitrate or equivalent gas producing material, the grains and particles of which are protected by a paste, consisting of a cereal or leguminous powder combined with nitroglycerin.

**420,642.**—Solidifying colored fire. H. O. Frank.

Pyrotechnic powders are converted into solid form by adding a small quantity of alcohol to the powdered ingredients, and mixing the whole thoroughly together in a water bath at about 93° until the mass is in a soft pasty condition, and then while still warm pressing the mass into molds, previously coated with vaseline, or other analogous substance.

**420,648.**—Insulating compound. J. B. Williams.

Consists of India rubber, paraffin, a resinous body, sulphur, silica or its equivalent, and oituminous matter, which is solid when cold.

**420,696.**—Process of manufacturing transparent fabrics. L. L. Perry.

Consists in first passing bleached cloth or fabric through a size composed of starch, borax, water and lard, then drying the fabric, then passing it through a mixture composed of paraffin wax, dissolved in naphtha, boiled linseed oil mixed with benzine, linseed oil varnish mixed with turpentine and starch, and water, then drying, then moistening and subsequently calendering or glazing the fabric.

**420,719.**—Apparatus for subliming sulphur. C. Dubois.

**420,749.**—Evaporating apparatus. L. W. Tracy.

**420,751.**—Gas washer. W. T. Walker.

**420,820.**—Process of restoring rubber. N. C. Mitchell.

Rubber scraps are mixed with heavy oil and calcium sulphide, and subjected to the action of live steam.

**420,821.**—Apparatus for use in restoring rubber. N. C. Mitchell.

**420,830.**—Process of recovering glycerine from spent lyes. C. L. Porter.

The process consists in first treating the soap liquid with sulphuric acid, next passing superheated steam directly through the liquid, next adding lead oxide, then cooling and separating from the separated salts, then again passing steam through the liquid over direct fire, next adding charcoal or other carbonaceous matter, then adding lime, and finally, completing the process by separating the lye from the glycerine.

**420,835.**—Apparatus for recovering alkali. Geo. Seiler.

**420,837.**—Process of making chlorine. E. Solvay.

A mixture of a calcined silicious clay-like material and a chloride is filled into a decomposing apparatus. Then gas or combustible dust is introduced midway into the decomposing apparatus, producing combustion in the apparatus, and finally a current of air is introduced into the lower part of the apparatus.

**420,877.**—Apparatus for dyeing. W. D. Jones.

W. R.

REGULAR MEETING, FEB. 7th, 1890.

Vice-President Breneman in the chair.

The minutes of the last meeting were read and accepted.

Dr. Geo. F. Barker, Dr. Edward Hart and Dr. J. T. McGill were unanimously elected members.

The following nominations were read : E. J. Milhau, 183 Broadway, as a member ; Francis J. Oakes, 85 Stone street, New York, as an associate member ; George Stiff, Long Island City, N. Y., as an associate member.

The following papers were read by the authors : "An Examination of the Meat of Poultry Fattened by the French Process," H. A. Mott, Jr., Ph. D.; "On the Formation of Anthraquinone under Peculiar Conditions," L. H. Friedburg, Ph. D.; "Some Lecture Experiments (with illustrations)," A. A. Breneman, S. B.; \* "Azainine, a new dye," J. H. Stebbins, Jr.

The resignation of Mr. T. S. Gladding was read and accepted.

The Committee on Reorganization was discharged.

The committee appointed in November, 1889, to canvass for papers for the JOURNAL was, on motion, instructed to report at the next meeting and file the report with the Secretary.

The meeting was then adjourned.

CHAS. F. McKENNA,  
Recording Secretary.

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\* Withheld from publication temporarily, by the author.



## ON THE FORMATION OF ANTHRAQUINONE UNDER PECULIAR CONDITIONS.

BY L. H. FRIEDBURG, PH. D.

(Read before the AMERICAN CHEMICAL SOCIETY, Feby. 7, 1890.)

Both the indophenin reaction, formerly used as a test for benzol<sup>1</sup>, and the phenanthraquinone reaction of Laubenheimer<sup>2</sup>, effected with toluol, have been shown by Victor Meyer<sup>3</sup> to be due, *not* to benzol and toluol, but to thiophene and methylthiophene respectively. The first suggestion of an experiment looking towards the isolation of thiophene was the fact that some benzol, obtained by distillation of benzoic acid<sup>4</sup> with lime, did *not* show the indophenin reaction<sup>5</sup>. This reaction consists in treating coal tar benzol with isatin and concentrated sulphuric acid, when deep blue indophenin  $C_{12}H_7NOS$  results.

But benzol and toluol, after proper treatment with concentrated sulphuric acid, will not show the indophenin or the phenanthraquinone reaction respectively<sup>6</sup>.

This latter reaction, also called the Laubenheimer reaction, was described by its discoverer in 1875 (*loc. cit.*) as follows :

“A few drops of toluol are added to a dilute solution of phenanthraquinone in glacial acetic acid. The mixture is cooled continually and drops of concentrated sulphuric acid are allowed to run into it. After a few minutes water is added. A coloring substance is precipitated, which, on shaking with ether, dissolves with a beautiful purple tint.”

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<sup>1</sup> A. von Baeyer, Ber. **12**, 1311 ; **16**, 1477 ; **18**, 2637.

<sup>2</sup> Ber. **8**, 224.

<sup>3</sup> Die Thiophengruppe ; Vieweg, 1888.

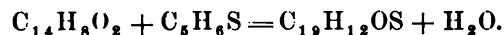
<sup>4</sup> From urine, from resin or from toluol.

<sup>5</sup> V. Meyer, (*loc. cit.*) pp. 1 *et seq.*

<sup>6</sup> Ber. **17**, 1338.

The indophenin reaction is caused by the presence of thiophene ( $C_4H_4S$ ) which exists in all coal tar benzol, while correspondingly, the Laubenheimer reaction is occasioned by  $\alpha$ -methylthiophene, called  $\alpha$ -thiotolene,  $C_4H_3SCH_3$ , contained in all coal tar toluol. The pure thiophene and thiotolene show the two described reactions most distinctly.

The analysis of the coloring matter prepared from phenanthraquinone,  $\alpha$ -thiotolene and conc. sulphuric acid, shows approximately the formula,  $C_{11}H_{12}OS$ , so that V. Meyer<sup>1</sup> writes the following equation for the formation of this body, which is precipitated in the shape of indigo blue flocks:



It is a dark blue powder which, on pressure, assumes a copper lustre. It is easily soluble in alcohol, benzol, chloroform and carbon disulphide, but insoluble in water. Heated alone, it does not show any characteristic behavior.

A remarkable result was shown, however, on combustion of the substance with lead chromate. At a comparatively low heat a *yellow vapor* was formed, which sublimed in the colder part of the tube (outside of the combustion furnace), in the shape of large golden yellow needles. These were free from sulphur, did *not* give the phenanthraquinone reaction, showed on resublimation the melting point of  $274^\circ C$ . and exhibited every other property of *anthraquinone*. The characteristic reaction of Claus<sup>2</sup> for anthraquinone was also obtained and finally the body was transformed into *alizarine*.

The phenanthraquinone that was used for the preparation of the above mentioned coloring substance had been newly prepared

<sup>1</sup> Die Thiophengruppe, p. 40.

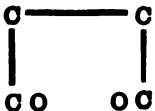
<sup>2</sup> Mix 1 mg. anthraquinone with some sodium amalgam, add absolute ether (free from alcohol) and shake. On now adding a few drops of water a red coloration ensues, which disappears again on shaking, in consequence of the admission of air. On adding absolute alcohol to the mixture of anthraquinone and sodium amalgam a green coloration sets in, disappearing on agitation with air. Both colors reappear on standing. (Claus, Ber. 10, 927.)

from its pure bisulphite compound and did *not* contain any anthraquinone.

V. Meyer<sup>1</sup> says: "It will be difficult to find an explanation for this peculiar pyrogenous reaction. It seems almost as if the methyl group of the thiotolene has to do with this formation of anthraquinone. The fact that the green coloring substance obtained from *thiophene*,<sup>2</sup> and phenanthraquinone under the same treatment did *not* lead to anthraquinone, favor this assumption.

In the following pages I offer an explanation of this peculiar formation of anthraquinone, and I shall also propose some experiments which will decide whether my theory is right or not. A careful study of V. Meyer's work on thiophene and its derivatives and an extended acquaintance with the behavior of aromatic compounds, particularly of those formed by condensation from the fatty series, lead me to regard this explanation as highly probable.

Before considering the main object of this paper, it may be well to glance briefly at the mode of preparation and the constitutional formula of thiophene, also to mention some of its properties. V. Meyer,<sup>3</sup> Volhard and Erdmann,<sup>4</sup> Paal,<sup>5</sup> also Paal and Tafel,<sup>6</sup> Tiemann and Haarmann,<sup>7</sup> have contributed methods for the synthesis of thiophene. According to these researches<sup>8</sup> many sub-

stances which contain the group ;  as for instance,

succinic acid, pyro-tartaric acid, acetonyl-acetone, laevulinic acid,

<sup>1</sup> Die Thiophengruppe, page 41.

<sup>2</sup> See pp. 30 and 43 of this paper.

<sup>3</sup> Ber. 16, 2176.

<sup>4</sup> Ib. 18, 454.

<sup>5</sup> Ib. 18, 367 and 2251.

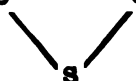
<sup>6</sup> Ib. 18, 456 and 688.

<sup>7</sup> Ib. 19, 1257.

<sup>8</sup> V. Meyer, die Thiophengruppe, p. 249.

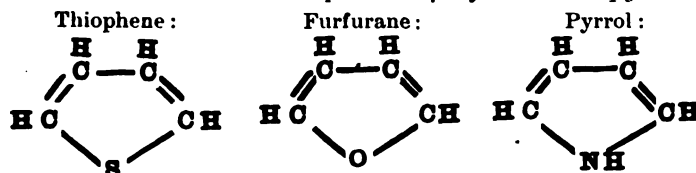
etc., when treated with phosphorus trisulphide,<sup>1</sup> yield thiophenes,

a complex group  $\text{O} \cdots \cdots \text{C}$  being formed from the two CO



groups. The best synthetical preparation of thiophene, one of practical value, is that of Volhard and Erdmann (*loc. cit.*), published in 1884. It consists in the treatment of sodium succinate with a *double* quantity of phosphorus trisulphide. This method, which has since been improved, yields fifty per cent. of the theoretical quantity. Thiophene thus prepared is sold at 130 marks per kilo.

V. Meyer<sup>2</sup> gives a discussion of the structural formula of thiophene, which leads him to compare it to *furfurane* and *pyrrol*.



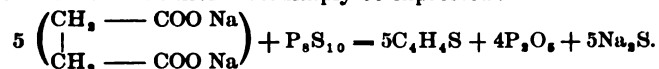
<sup>1</sup> Which is *not* to be considered a real chemical combination, but a fused mixture of the components in the proportion of  $\text{P}_8$  to  $\text{S}_8$ .

In order to understand this formation, we must assume that five molecules of sodium succinate would be acted upon by a mixture of

$\text{P}_8\text{S}_{10}$  (very nearly  $4\text{P}_8\text{S}_8$ ).

Because *one* molecule of sodium succinate would have to lose  $\text{O}_4$  and  $\text{Na}_8$ , while one atom of sulphur would take the place of these.

The reaction could then most simply be expressed :



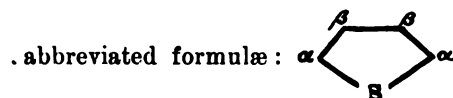
The molecular weight of sodium succinate and of  $\text{P}_8\text{S}_8$  are very nearly the same, being as 162 to 158.

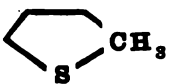
Since phosphoric anhydride cannot easily be supposed to exist under these conditions along with either sodium succinate or sodium sulphide, a more complicated reaction will take place, leading to sulphur compounds higher than thiophene. To avoid this may be the reason for the practical prescription of using  $2\frac{1}{2}$  times the amount of  $\text{P}_8\text{S}_{10}$  indicated by the equation.

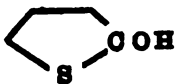
L. H. F.

<sup>2</sup> Die Thiophengruppe, p. 80, *et seq.*

To facilitate the study of the substituted thiophenes, he uses the

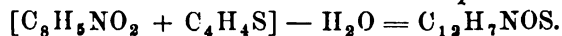


Thus the methyl thiophene above mentioned as *α-methylthiophene* or *α-thiotolene*, has the constitution: 

while the corresponding thiophenylaldehyde, which will be referred to later, would be: 

The properties of thiophene are the following: It is a colorless, clear liquid, boiling at 84° C. (Benzol boils at 80.5° C.) It has a feeble and not very characteristic odor. It is not miscible with water. It does *not* solidify in a mixture of ice and salt. Concentrated sulphuric acid dissolves it in the cold with dark brown coloration; later the mixture evolves hydrogen sulphide, then sulphur dioxide, finally the mass thickens, and when water is added a thick, gray, amorphous precipitate is formed, which is insoluble in all liquids. The reaction between thiophene, isatin and conc. sulphuric acid, forming by condensation, according to A. v. Baeyer (*loc. cit.*), the beautifully blue dyestuff indophenin, is the most delicate reaction, indicating the presence of the smallest traces of thiophene. According to A. v. Baeyer, the reaction takes place thus:

*Indophenin.*



Thiophene and phenanthraquinone show the Laubenheimer reaction, when *ether* is replaced by *chloroform*, the dye formed dissolving in the latter with deep emerald green color.<sup>1</sup>

<sup>1</sup> V. Meyer, die Thiophengruppe, pp. 24 and 25. See also pp. 28 and 43. of *this* paper.

Thiophene is not attacked when distilled over metallic sodium. In physiological action it differs from benzol.<sup>1</sup>

Approaching now the main object of our discussion, which is, to explain the formation of anthraquinone from the dye  $C_{14}H_8OS$ ,<sup>2</sup> when this latter is heated with lead chromate, we find, *a priori*, three possible cases of decomposition.

I.—The anthraquinone is exclusively formed out of the phenanthraquinone residue, by rearrangement of the atoms within the molecule and oxidation.

II.—Both, the phenanthraquinone residue *and* the thiotolene residue participate in building up anthraquinone.

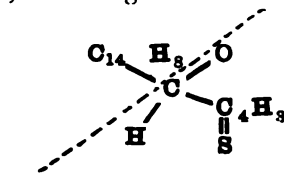
III.—The *thiotolene residue only* is transformed into anthraquinone, being at first and intermediately oxidized to thiophene aldehyde.

I shall only consider the third case, which also implies the formation of anthraquinone out of  $\alpha$ -methylthiophene.

The following two equations express the supposed formation :

1.  $[3C_6H_4S] + [6O]$  minus  $[CO_2 + 3H_2S + 2H_2O] =$   
 $C_{14}H_8O_2$ . Anthraquinone
2.  $[3C_6H_4OS]$  minus  $[COS + 2H_2S] = C_{14}H_8O_2$ .

In constructing these two equations I have, of course, recognized the fact that we do not find a *whole* molecule of methylthiophene in the blue dye obtained from phenanthraquinone plus methylthiophene minus water, but probably the residue  $C_6H_4S$  very closely linked to one oxygen atom, which binds the carbon of the methyl group to the phenanthraquinone, while a second valency of this same carbon atom is directly linked to the phenanthraquinone residue, according to the following formula :



<sup>1</sup> Die Thiophengruppe, p. 26 ; and A. Heffter, Archiv für die gesammte Physiologie, **39**, 420.

<sup>2</sup> From  $\alpha$ -thiotolene, phenanthraquinone and conc. sulphuric acid.

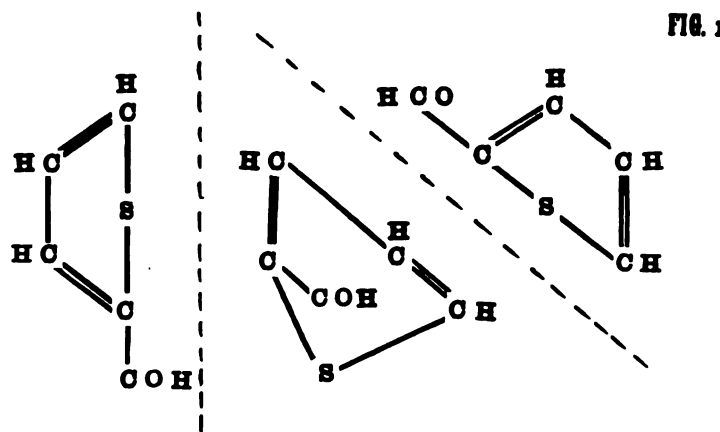
The splitting off of thiophene aldehyde is then indicated by the dotted line.

Further, it will be shown how anthraquinone may be formed from thiophenaldehyde, transitorily existing in our reaction as the formula indicates. I will only point out here, that *simultaneously* with such a formation, the phenanthrene residue  $C_{14}H_8$  also might suffer a rearrangement of its nucleus and then be oxidized by the lead chromate to anthraquinone, so that a formation of this latter might take place according to case III. and case I. together.

But the main interest being attached to case III., since it shows the possibility of a transition from a thiophene derivative to an anthracene derivative, I will consider it exclusively.

Let us then look at the inner mechanism, as indicated by equation 2.

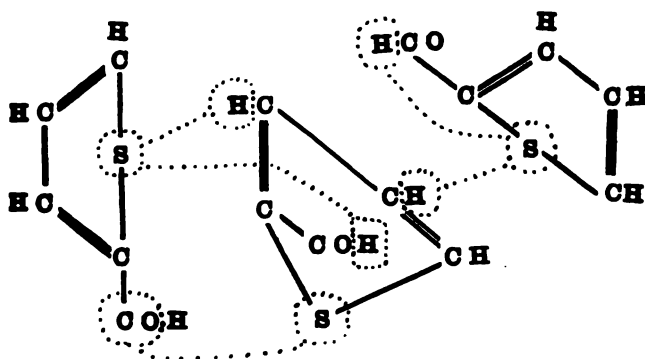
To this end I arrange on the paper the formulæ<sup>1</sup> of three thiophenaldehyde molecules in such a manner that the supposed formation of anthraquinone may be more easily foreseen.



<sup>1</sup> *Ladenburg, Theorie der aromatischen Verbindungen* (Vieweg, 1876), page 23, says: In modern chemistry the formula of a substance is an expression which gives not only an account of the composition and the true molecular weight of that substance, but which *also* indicates a definite view of the manner in which the atoms, forming that molecule, are linked together.

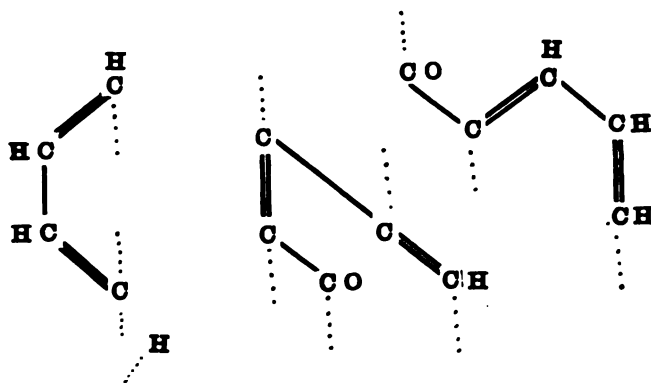
We may now remove from these three molecules of thiophenaldhyde, two of hydrogen sulphide and one molecule of carbon oxy-sulphide in the following manner :

FIG. 2



The remaining residues, in which the unsaturated valencies are indicated by dotted lines, would then face each other thus :

FIG. 3

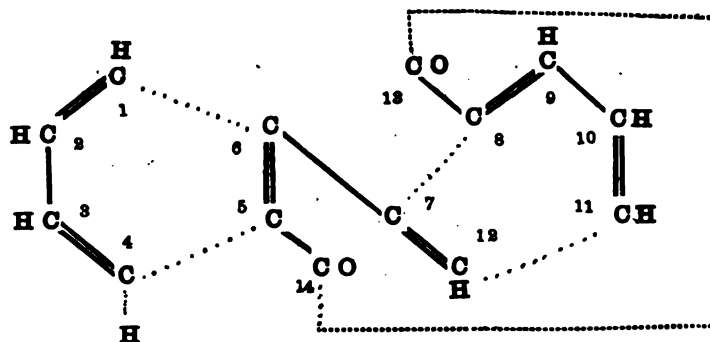


Now in order to do justice, in a manner, to Kekulé's repeatedly expressed demand <sup>1</sup> ("in imagining the construction of such for-

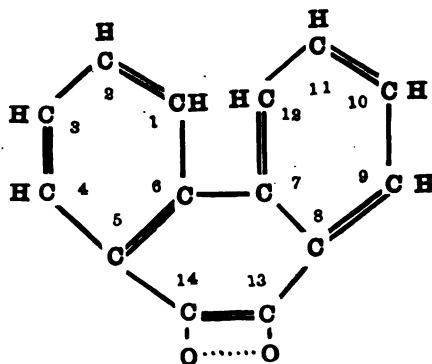
<sup>1</sup> See page 35 of this paper, foot note.



**FIG. 4**



**FIG. 5**



necessary at this point to give a correct picture of anthraquinone, this will be done later. I restrict myself here to showing merely that a similar ring can easily be formed out of thiophenaldhyde. The forms which would correspond to equation 1, are quite

# ON THE FORMATION OF ANTHRAQUINONE.

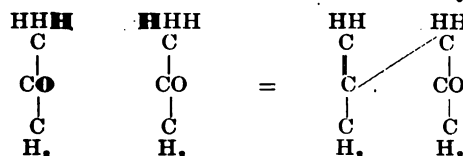
analogous to the ones given just now, only we have to start from methylthiophene under oxidizing conditions. In relation to the arbitrary abstraction of  $\text{H}_2\text{S}$  and of  $\text{COS}$ , we must not forget that we work in the presence of lead and of available oxygen, and that I only assume, that the *elements* which can form those two compounds are taken away, so as to form finally water, carbon dioxide and lead sulphate.

The decisive experiment which I propose, is to conduct thiophenaldehyde (or methylthiophene) over fused lead or lead oxide, at a gentle heat, perhaps also over mercuric oxide, and only if that experiment should not produce anthraquinone, to take lead chromate.

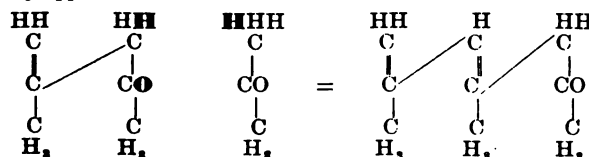
But here I must suggest an important consideration.

*Intermediate* products have always been of great weight in the study of the formation of aromatic nuclei. I merely instance phorone and mesityloxyde in the formation of mesitylene from acetone, as one example.<sup>1</sup> I have thought, that it might lead more easily to the point, if the possibility of formation of intermediate products were considered also in this case. One such product for example, could be formed from *two* molecules of thiophenaldehyde, from which the elements of one mol.  $\text{H}_2\text{S}$  and of one mol.  $\text{COS}$  would be eliminated. Fig. 6 indicates, in a

<sup>1</sup> Two mols. of acetone minus one mol. of water =  $\frac{\text{Mesityloxyde}}{\text{C}_6\text{H}_{10}\text{O}}$

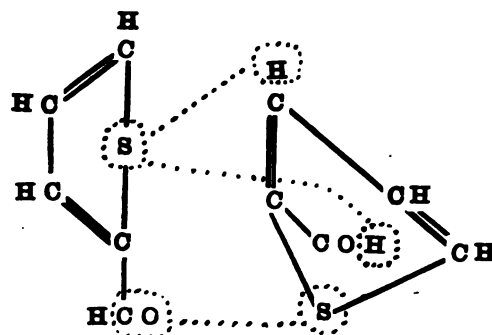


One mol. of mesityloxyde plus one mol. of acetone minus one mol. of water =  $\frac{\text{Phorone}}{\text{C}_8\text{H}_{14}\text{O}}$  (see also Kekulé, Ber. 2, 368).



manner perfectly analogous to that of Fig. 2 how this elimination might be supposed to take effect.

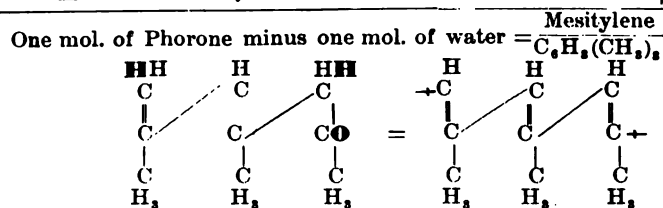
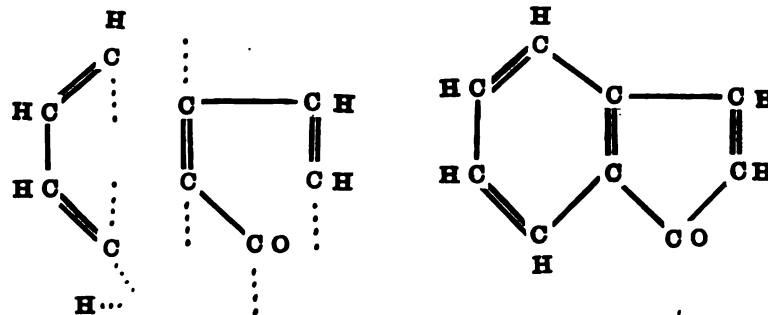
FIG. 6



The remaining residues are shown in Fig. 7 with the free valencies indicated by dotted lines, while in Fig. 8 those valencies are mutually saturated :

FIG. 7

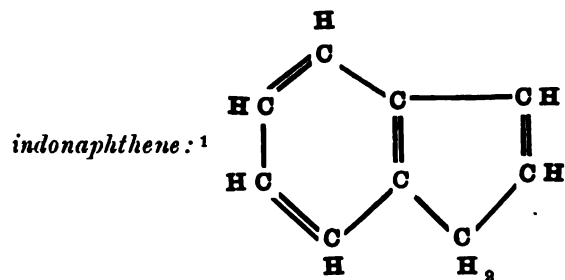
FIG. 8



[Note.—In the last three equations (footnotes pp. 35 and 36) symbols in faced type show atoms eliminated. The daggers mark the two carbon atoms joined to one another by a single bond.]

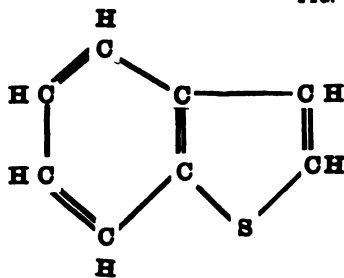
Such an intermediate body would be of the highest interest. As a comparison for it we may look to the also hypothetical

FIG. 9



We might call this new hypothetical substance *ketonaphthene*, indicating the presence of a ketonic group (CO). There are two other compounds which are very properly drawn into this comparison, the one is the hypothetical *thionaphthene* of V. Meyer:<sup>2</sup>

FIG. 11



the other, a substance prepared by A. W. Hofmann<sup>3</sup> (called by V.

<sup>1</sup> Derivatives of these hypothetical bodies have been prepared; see W. Roser, Ber. 20, 1574; also 16, 926; 1041; 2261; 18, 190; further, A. v. Baeyer and W. H. Perkin, Jr., Ber. 17, 125; see likewise Perkin, Ber. 16, 208, 1787, 2136.

<sup>2</sup> Thiophengruppe, p. 252.

<sup>3</sup> Ber. 13, 224.

Meyer a quinoline of the thiophene series, and by Hofmann,<sup>1</sup>—who places it parallel with the thiophene group, and who has prepared quite a number of derivatives—*methenylamidophenylmercaptan*) which has this constitution :

FIG. 12

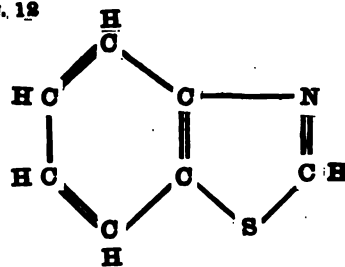
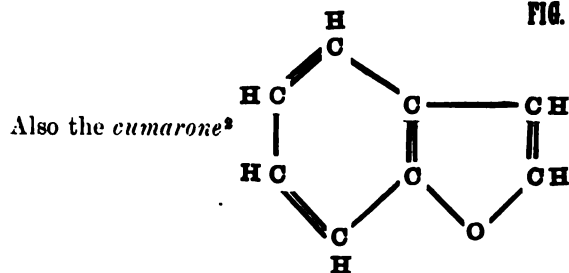
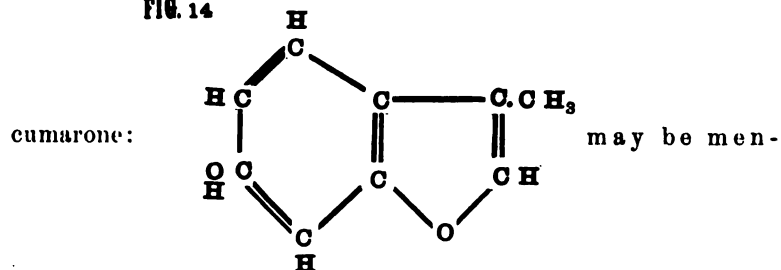


FIG. 13



and derivatives of the same, as, for instance *Hantzsch's*<sup>3</sup> oxymethyl

FIG. 14



<sup>1</sup> Ber., 12, 1127; 13, 9; 12, 1128; 19, 1811; 20, 1790; 20, 2257; 12, 1129, etc., etc.

<sup>2</sup> Beilstein, Handbuch d. org. Chemie, 1888, v. 3, 442.

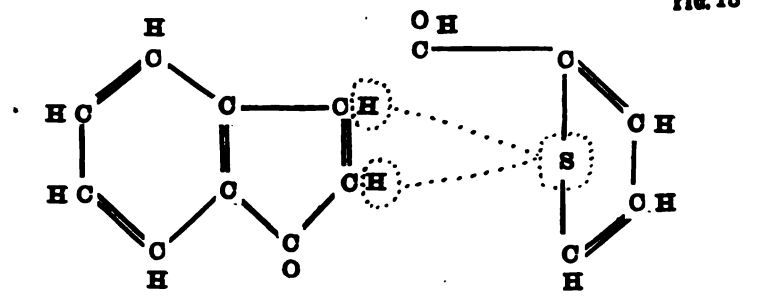
<sup>3</sup> Ber. 19, 2929.

tioned here'. Altogether the existence of the intermediate product, to which our investigation has brought us, and which I have proposed to call *ketonaphthene*, can be looked upon as possible. Such a substance may yet be prepared, and when prepared it will not stand alone.

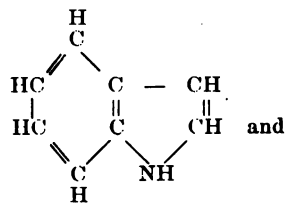
It is now but one step to show how, by way of this intermediate product, anthraquinone may be finally produced from thiophen-aldehyde.

Let us suppose that the so formed ketonaphthene is acted upon (under the given conditions) by one mol. of thiophen-aldehyde and that the elements of one mol. of  $H_2S$  are expelled in consequence. We would, on the same principle as in former diagrams, arrive at the three formulæ :

FIG. 16



Of course also the indol:



the hydrindonaphthene:

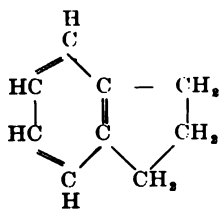


FIG. 16

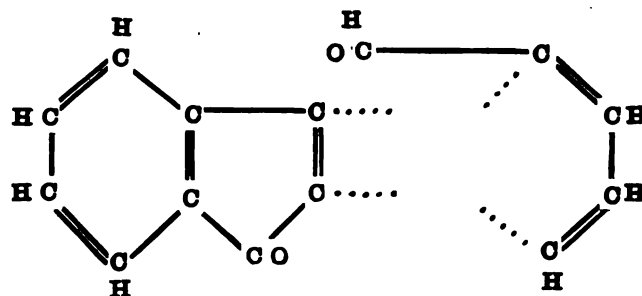
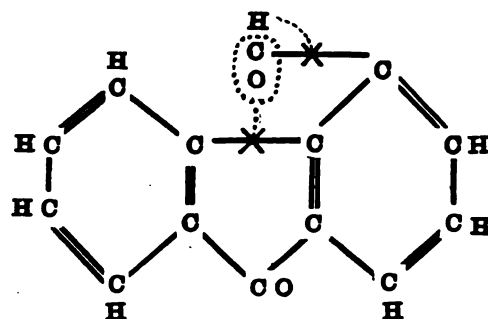


FIG. 17

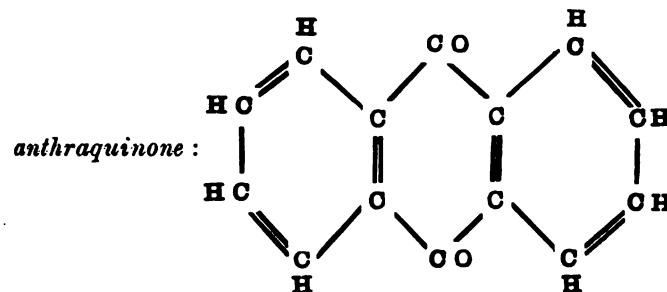


<sup>1</sup> In order to understand how this construction can lead to anthraquinone we have to suppose that the two crossed valencies are ruptured, that consequently the hydrogen atom of the aldehydic group (COH) is more closely attracted by that carbon atom to which this group was linked, and that the two carbonyl groups

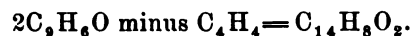
<sup>1</sup> This Fig. 17 would represent a substance which we might call benzophenecarbaldehyde, an unknown compound isomeric with anthraquinone, etc. But such ketone-aldehydes seem to be incapable of existence in the free state. So, for example, the aceto-acetic aldehyde,  $\text{CH}_3 - \text{CO} - \text{CH}_2 - \text{COH}$ , in reference to which see, Ber., 21, 1144.

(CO) enter into a union, peculiar to quinones. We thus arrive at

FIG. 18



But much simpler yet we shall obtain this same figure of anthraquinone if we assume that this is formed from two mols. of *ketonaphthene* :



This formation would be quite analogous to that of naphthalene from two mols. of benzol, or of anthracene from naphthalene.

The following formulæ demonstrate the supposed condensation :

FIG. 19

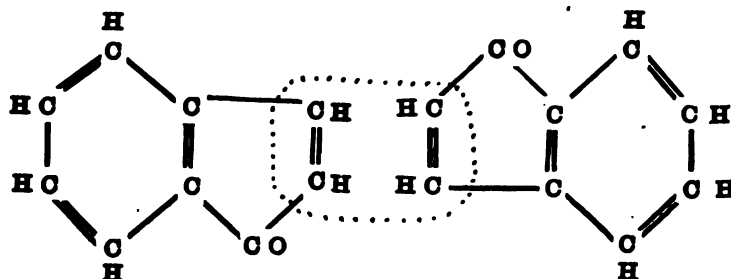
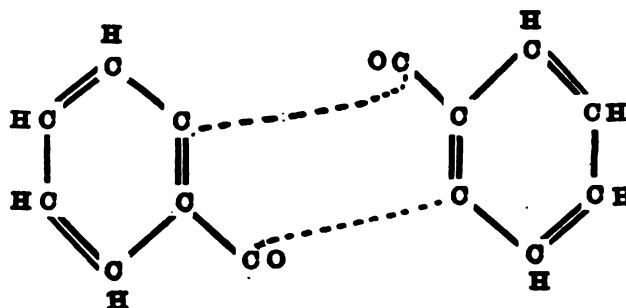




Fig. 20



Here then at least it is not required to rearrange any bonds, which ~~was~~ necessary in the condensation of ketonaphthene plus thiophenaldehyde to form anthraquinone.

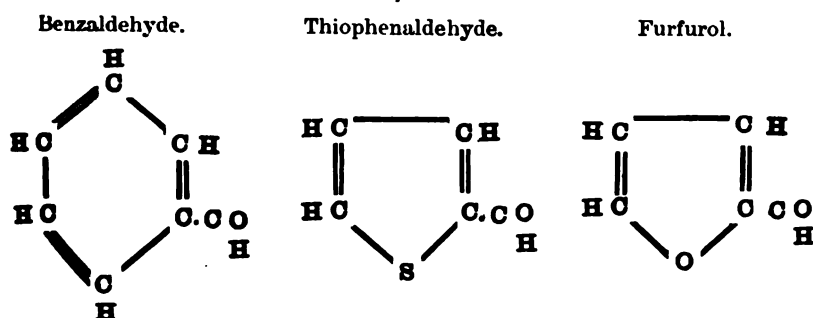
I have supposed in the above that the blue dye formed from phenanthraquinone, methylthiophene and conc.  $\text{H}_2\text{SO}_4$  under elimination of water, permits the splitting off of thiophenaldehyde, which on its part can be supposed to form anthraquinone in two ways, as just demonstrated. An experiment should be performed, under carefully devised conditions, by means of which thiophenaldehyde would really be obtained from that blue dye. This would be a good support for the theory which I have developed and would also be a highly interesting case of oxidation of methylthiophene by means of phenanthraquinone to thiophenaldehyde. The preparation of this latter substance is not now an easy matter. Starting from thiophene, according to V. Meyer<sup>1</sup>, acetothienone<sup>2</sup> has first to be prepared by means of acetylchloride and aluminium chloride. From acetothienone the thienylglyoxylic acid<sup>3</sup> is formed by means of oxidation in an alkaline permanganate solution; finally the thienylglyoxylic acid is subjected, in portions of five grammes, to destructive distillation in a current of carbon dioxide, when thiophenaldehyde results. This substance (which

<sup>1</sup> Die Thiophengruppe, pp. 155; 219 and 220; 151.

<sup>2</sup>  $\text{C}_4\text{H}_3\text{S}-\text{CO}-\text{CH}_3$ .

<sup>3</sup>  $\text{C}_4\text{H}_3\text{S}-\text{CO}-\text{COOH}$  [the glyoxylic acid being  $\text{HCO}-\text{COOH}$ ; or,  $(\text{OH})_2\text{HC}-\text{COOH}$ .]

resembles benzaldehyde more closely than it does furfural, even in possessing its odor) might, if the proposed experiment should prove a success, be prepared therefore in a simpler way.



Finally I will state that, in the explanation offered above for the formation of anthraquinone from thiophenylaldehyde, I have taken into full account the fact (also mentioned here<sup>1</sup>) that *no* anthraquinone results from the treatment with lead chromate of the green coloring substance resulting from thiophene, phenanthraquinone and conc.  $\text{H}_2\text{SO}_4$ ; that, therefore, as V. Meyer, expressly remarks, (*loc. cit.*), it seems to be the methyl group of methylthiophene, which promotes the formation of anthraquinone. The experiments by means of which I hope to sustain this theory will be performed soon, and I shall report on the same as early as possible.

COLLEGE OF THE CITY OF NEW YORK,  
February 7, 1890.

<sup>1</sup> See pages 28 and 30 of this paper.

AN EXAMINATION OF THE MEAT OF POULTRY  
FATTENED BY THE FRENCH PROCESS.

BY PROF. HENRY A. MOTT, PH.D., LL.D.

Having had occasion to examine the French Process for the Fattening of Poultry, it occurred to me that the result of my investigation may prove of interest.

By this process chickens, which have been accustomed to run at large and obtain such food as they can find, are placed in separate compartments and secured, the compartments being arranged on a large revolving table, with one tier above the other.

The chickens are fed one at a time by the keeper, who rotates the table, thus bringing the chickens one after another in front of him. A tube having an appropriate nozzle is inserted in the mouth of the chickens and passed into the throat, through which tube a definite amount of food is injected into the chicken's crop (not into the stomach). At first, only a small quantity of food is thus fed to the chickens, but toward the end of three weeks, the time required for the fattening process, the quantity of food is increased.

The food consists of

Buttermilk.....	30.0 per cent. by <i>volume</i> .
Corn meal.....	25.0 " "
Buckwheat meal.....	12.5 " "
Barley meal.....	7.5 " "
Water (sufficient for the right consistency).....	25.0 " "
	<hr/> 100.0 per cent.

During the first week, on an average 70.5 c. c. (4.3 cu. in.) of this food is fed three times a day; during the second week 93.4 c. c. (5.7 cu. in.) is fed at a time, and during the third and last week 129 c. c. (7.9 cu. in.) of food is fed three times daily.

The establishment is always kept dark, but perfectly ventilated, the object being to produce whiter meat and prevent restlessness, which would arise if the chickens could observe their surroundings.

After fattening over 250 chickens by this process, I selected three for investigation; I also secured in the market three Philadelphia and three Western chickens. I roasted, broiled and boiled one of each, with the following results:

CLASS OF CHICKEN.	WEIGHT AFTER BEING PICKED.			WEIGHT AFTER BEING DRESSED.			WEIGHT AFTER BEING COOKED.		
	Gms.	Lbs.	Oz.	Gms.	Lbs.	Oz.	Gms.	Lbs.	Oz.
<i>For Roasting.</i>									
Western chicken .....	1577.3	3	8	1247.1	2	12	793.5	1	12
Philadelphia chicken ..	1360.5	3	0	1020.4	2	4	680.1	1	8
French fattened chicken	1577.2	3	8	1133.7	2	8	680.1	1	8
<i>For Broiling.</i>									
Philadelphia chicken ..	1024.4	2	4	734.7	1	10	566.8	1	4
French fattened chicken	1133.7	2	8	852.6	1	14	648.5	1	7
<i>For Boiling.</i>									
Western chicken .....	1360.5	3	0	1020.4	2	4	734.7	1	10
Philadelphia chicken ..	1473.8	3	4	1020.4	2	4	793.5	1	12
French fattened chicken	1587.1	3	8	1133.7	2	8	793.5	1	12

CLASS OF CHICKEN.	LOSS OF WEIGHT IN COOKING.	TOTAL LOSS IN WEIGHT.	PERCENTAGE OF WATER IN COOKED BREAST.
<i>For Roasting.</i>			
Western chicken .....	36.37%	50.0%	57.57%
Philadelphia chicken ..	30.56%	50.0%	64.57%
French fattened chicken	40.00%	57.15%	64.18%
<i>For Broiling.</i>			
Philadelphia chicken ..	23.08%	44.45%	-- --
French fattened chicken	23.34%	42.50%	-- --
<i>For Boiling.</i>			
Western chicken .....	27.78%	45.84%	64.96%
Philadelphia chicken ..	22.23%	44.04%	53.84%
French fattened chicken	30.00%	50.0%	66.66%

The breast of the Western chicken when cooked was yellowish-white, tough, fibrous and stringy and difficult to masticate.

The breast of the Philadelphia chicken was cream-white, tender, but stringy, at the same time was easily masticated.

The breast of the French fattened chicken was pure white, homogeneous, not fibrous or stringy; very mellow, exceptionally tender, of fine delicate flavor and masticated without effort.

The meat on the second joint of the French fattened chicken was not so dark as the meat on the similar joint of the Western or Philadelphia chicken. It was found to be more juicy, possessed of more delicate flavor, and was more readily digested than either of the others.

The percentage of fat in relation to the nitrogenous matter is less in the meat of poultry than in the meat from mammals, and hence chicken meat is not quite as readily digested. The blood also differs considerably, but as chicken meat contains three times as much phosphates as the flesh of mammals, and as phosphates contribute to the regeneration of the nervous system, it is superior in this particular.

The ratio in which the nitrogen in food should exist as regards the carbon is as 1 to 16. There will then be generated by the oxidation of the carbon sufficient heat to maintain the normal temperature of the body during the time required for the digestion of the nitrogen-containing food.

If we call the meat of the chicken (less the fat) the nitrogen-containing food, then the more nearly the percentage of fat (represented by carbon) approaches the required ratio, the better will the normal temperature of the body be maintained during the process of digestion and the more easily will the meat be digested. If the breast of the chicken, devoid of fat, was eaten alone, whilst it would digest in time, the temperature of the body would be reduced and, if continued *exclusively*, would in a short time produce starvation and death. Just as the proportion of fat to the meat approaches the desired ratio, in the same proportion does it approach a more perfect food.

It becomes necessary therefore to know the percentage of fat the meat of the chicken contains in each case, and I have made the following analysis to determine this factor.

The breast of a Western, Philadelphia and French fattened chicken was taken before being cooked and submitted to analysis. As the raw meat is covered with a skin attached to which is the layer of fat, which on cooking permeates to a greater or less extent the meat, and is to some extent retained next to the meat and eaten with the same, this layer was detached and analyzed.

From the Western Chicken,-----3.01% of Fat was obtained.

“	Philadelphia Chicken, 10.7%	“	“
“	French fattened “ 64.76%	“	“

The difference in these results speak for themselves. It may, however, be well to remark that the French fattened chicken is enveloped by a layer of rich fat, which on partially melting in the process of cooking, permeates the meat, thus enhancing its value and at the same time furnishing a rich gravy, as the loss in weight in the first table clearly demonstrates.

It is a well established fact that exercise is unfavorable to fatty deposits; chickens that are allowed to run about do not become fat to the same extent as those confined at rest.

The distinguished English physician, Dr. Pavy, says: “The fattening of poultry for the table forms in some parts of the country an extensive branch of industry, and the improvements that are effected in the quality, equally as regards tenderness and flavor as size of the bird is exceedingly striking.”

The art, therefore, of fattening chickens consists in keeping them at rest, and feeding them with an abundance of easily digestible and appropriate fattening food, and subjecting them to this process for about three weeks before killing them for edible purposes. Experiment has shown that if the chickens are kept four or five weeks they become feverish and sickly, but if the time does not exceed three weeks, the desired result is obtained.

As the best food, care and attention is given to chickens when being fattened by the French process, it is no wonder that the flesh of such chickens, when cooked, is more tender, of more delicate flavor and more easily digested than the cooked flesh of chickens not so fed.

It is thought by some that the artificial feeding of chickens by the French process is identical with the process employed to obtain “*foie gras*” in the goose. This is an error, for in the case of the goose the process as given by Dr. Pavy is as follows: “Morning and evening, maize or Indian corn previously soaked in water, is crammed down the bird’s throat to repletion; during the day it ‘drinks and guzzles in the water before it,’ which con-

tains fragments of charcoal and salt. The liver of the goose is by this process increased in weight up to one to two pounds."

In the case of the French process for fattening chickens, the food given is *ground* meal, etc., mixed with the right proportion of milk and water, so as to facilitate digestion. In consequence of which, the chickens increase nearly forty per cent. in weight, the fat and meat being uniformly distributed over the body, and the liver not being enlarged *at all* as in the case of the goose.

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### SOME LECTURE EXPERIMENTS.

BY A. A. BRENNEMAN.

1. *The dissociation of soap by water.*

A well filtered alcoholic solution of soap containing a little phenolphthalein is poured carefully into a glass cylinder half filled with distilled water, which also contains phenolphthalein. The line of contact of the liquid is colored bright red, and, on carefully stirring with a long rod, a pink flush is diffused through the mixed liquids. As both are free from color before contact the liberation of alkali by the water is plainly shown, and the theory of the action of soap is thus illustrated. The alcohol may be of fifty to eighty per cent., and should contain a large quantity of soap in solution. The cylinder is tilted at forty-five degrees in pouring in the soap solution so that the layers of liquid may be distinct.

2. *Dissociation of ammonium chloride by heat.*

The following experiment is easily performed and requires much less apparatus than such as require the separation of the dissociated constituents by diffusion through a porous cylinder. It depends simply upon the greater solubility of ammonia gas in water as compared with gaseous hydrochloric acid.

Into a long necked, round bottomed Bohemian flask is put three to five grms. solid  $\text{NH}_4\text{Cl}$ , and the flask is heated over a gas lamp (best a triple burner), until the solid has nearly disappeared and the bulb of the flask is filled with transparent gas.

A glass rod having a strip of moistened red litmus paper wound spirally around it for four inches of its length is then introduced as far as the bulb. On withdrawing it after ten seconds the paper will be entirely blue and, if still moist, will then turn red on quickly exposing it to the fumes issuing from the mouth of the flask.

After cooling, the residual  $\text{NH}_4\text{Cl}$  may be dissolved in water and tested with litmus to show its faintly acid reaction. Ordinary sublimed  $\text{NH}_4\text{Cl}$  is faintly acid, but a sample purified by solution and recrystallization will be so nearly neutral that the greater acidity of the sample from the flask will be quite apparent. If, during the heating of the flask, a thick dry rod, previously cooled by ice or ether, be inserted into the transparent gases of the heated flask, heavy clouds of  $\text{NH}_4\text{Cl}$  are produced.

*3. Opaque soap bubbles for many forms of gas experiment.*

Two flasks, arranged like gas-washing bottles and tied together so as to be handled as one, are filled to the depth of 1.5 c. c. with strong  $\text{NH}_3$  and  $\text{HNO}_3$  respectively. The long tube of each bottle reaches to within one cm. of the surface of the liquid but does not touch it; the short tube ends just below the stopper in each bottle. On forcing any gas first through the long tube into the bottle containing  $\text{HNO}_3$  and from that through the connecting tube against the surface of the  $\text{NH}_3$  solution in the other flask, dense, white fumes of  $\text{NH}_4\text{NO}_3$  are produced and bubbles may be blown with the gas from the second bottle. Nitric acid is preferable to  $\text{HCl}$  as fumes of  $\text{NH}_4\text{Cl}$  soon choke the exit tube, while  $\text{NH}_4\text{NO}_3$  is deliquescent in presence of moist  $\text{NH}_3$  gas. Also, the gas must pass *last* through the  $\text{NH}_3$  bottle as otherwise nitric acid fumes will be in excess in the mixture, and the soap will be decomposed, preventing formation of bubbles. Such bubbles are more readily visible by daylight or gaslight and much more satisfactory for use before large audiences. The quantity of vapor added is too trifling to affect the density of the gas, and the properties of weight, combustibility, etc., may be illustrated as usual. With  $\text{CO}_2$ , however, the rapid formation of ammonium carbonate in the second bottle necessitates a little practice in manipulating the apparatus.



## ABSTRACTS.

### Abstracts of American Patents Relating to Chemistry.

*(From the U. S. Patent Office Gazette.)*

*Issued February 11th, 1890.*

**420,945.**—Process of reducing metallic oxides to the metallic state. L. G. Laureau.

The process consists in mixing hydrocarbon gas with air in such proportion that the oxygen of the air will transform the carbon of the hydrocarbon into carbon monoxide, subjecting the mixture to the temperature of combination of oxygen and carbon and such higher temperature as the ore reduction calls for, and injecting the carbon monoxide, hydrogen and nitrogen thus formed into the mass of ore.

**421,009.**—Method of etching and oxidizing gold plated silverware. G. Myrick and W. Roller.

**421 010.**—Method of etching gold plated silverware. G. Myrick and W. Roller.

**421,029.**—Apparatus for distilling wood. E. Koch.

**421,081.**—Process of extracting silver from copper ores, mattes and other copper products. R. Pearce.

The finely pulverized ore or matte is mixed with two per cent. of sodium or potassium sulphate, and the mixture is roasted, after which the silver sulphate is obtained by leaching with hot water.

**421,046.**—Process of refining copper. J. Garnier.

Copper ores, desulphurized by subjecting them, in the presence of carbon, to fusion in a basic lined furnace in the presence of basic slag, the basic slag used being composed of about seventy per cent. of base and thirty per cent. of silica.

**421,049.**—Sulphonating rosaniline. E. D. Kendall.

Rosaniline is heated dry with sodium or potassium bisulphate.

**421,058.**—Drying apparatus. C. Sentz.

**421,076.**—Binary fluid. G. H. Holgate.

Consists of a liquefied mixture of anhydrous sulphur dioxide and carbon dioxide.

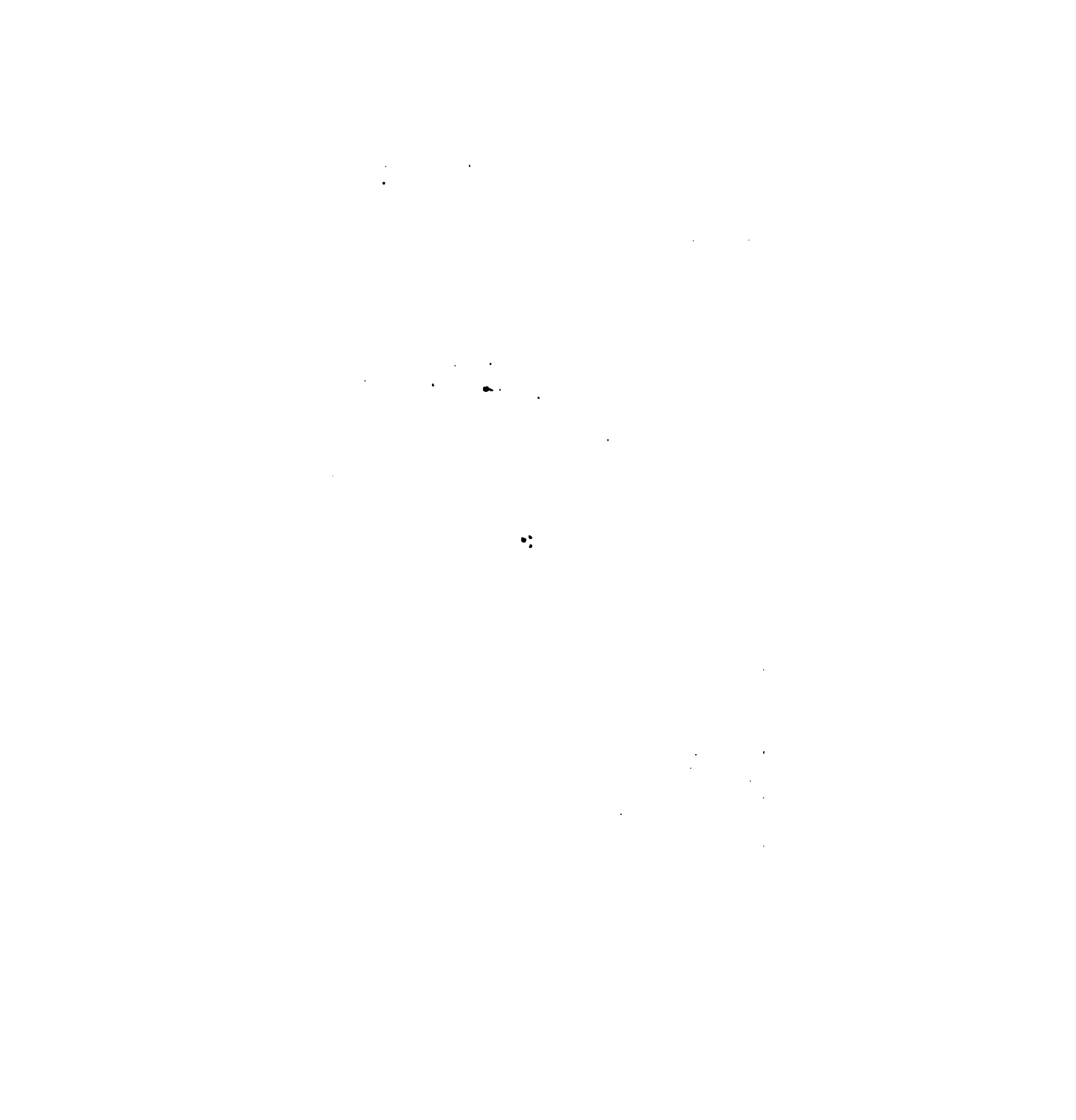
- 421,093.**—Oil Filter. C. G. Bryant.  
**421,161.**—Method of lining metallic vessels with lead. T. B. Burgess.  
**421,163.**—Vacuum evaporator. W. H. Collings.  
**421,172.**—Compound plaster. T. Jones.  
 Consists of lime, silica, gypsum and potassium bicarbonate.  
**421,201.**—Sulphur burner. S. Smith.  
**421,223.**—Detergent. C. P. Andersen.  
 Consists of a decoction of quillaia bark with soap, haematin, and potassium bicarbonate.  
**421,229.**—Composition of Paint. N. A. Bibikov.  
 Consists of sodium silicate, potash, pulverized mica and lime.  
**421,238.**—Filter. A. L. Bush and W. C. Clark.  
**421,299.**—Art of manufacturing coke. H. Mueller.  
**421,360.**—Composition for paint. D. S. Robinson.  
 Consists of pulverized slate, rosin, crude hydrocarbon oil, linseed oil and Japan drier.

*Issued February 18th, 1890.*

- 421,431.**—Process of producing caramel malt. L. Ramsel.  
**421,503.**—Filtering press. D. Licht.  
**421,521.**—Filter. J. Seabrooks.  
**421,564.**—Stove polish. B. C. Frobisher.  
 Consists of water, sodium silicate, crude plumbago, glycerin and manganese dioxide.  
**421,583.**—Coke oven. I. N. Knapp.  
**421,640.**—Blue azo dye. A. Weinberg.  
 Is prepared by first combining diazo compounds with the oxy-ethers of alphanaphthylamine or their sulpho acids, forming as intermediate products the sulpho acids of compounds of the general formula :  

$$R_1-N=NC_{10}H_7(OR)(NH_2)$$
 (where R, NH<sub>2</sub> stands for the aromatic amido compound, R for the alkyl group), and afterward diazotizing these basic compounds and reacting with the diazo-azo derivatives upon amines or phenols.  
**421,662.**—Explosive compound. B. Broncs.  
 Consists of a double salt of sodium picrate with other picrates, potassium nitrate, saccharine matter, a gummy or resinous substance and soot.  
**421,753.**—Explosive compound. H. Orth.  
 Consists of the double picrate of sodium and barium or lead, combined with nitrated naphthalin.  
**421,830.**—Preparation of flour from curd of milk. W. Gerbel.  
**421,847.**—Mordant. C. Wachendorff.  
 Consists of chromium chloride.

W. R.



REGULAR MEETING, MARCH 7th, 1890.

Vice-President Breneman in the chair.

The minutes of the February meeting were read and adopted ; also the minutes of the Directors' meeting held March 6th.

George Stiff, Long Island City, N. Y., and Francis J. Oakes, 85 Stone street, New York, were unanimously elected as Associate Members.

The following papers were read : "On the Determination of the Firing Points of Various Explosives," by Prof. C. E. Munroe (read by the secretary) ; "The Action of Nitrous Anhydride on Organic Bodies," by L. H. Friedburg and J. A. Mandel ; "Hydrogen Dioxide, its Manufacture and Applications," by A. Bourgougnon.

The resignations of Dr. Koenig and Dr. Adler were read and accepted. The editor reported from the Committee on Papers and Publications that the JOURNAL was now up to date.

The meeting was then adjourned.

CHAS. F. McKENNA,  
Recording Secretary.

## ON THE ACTION OF NITROUS ANHYDRIDE UPON ORGANIC COMPOUNDS.

BY L. H. FRIEDBURG and JOHN A. MANDEL.

(*Second Paper.*)

Before taking up the study of the reaction of nitrous anhydride upon benzaldehyde, we submitted diphenyl and benzonitrile to the same reaction under the conditions already given.

*Diphenyl and Nitrous Anhydride.*—Diphenyl was prepared by the method of Berthelot,<sup>1</sup> as modified by G. Schultz<sup>2</sup> and by H. Hübner.<sup>4</sup> A piece of  $\frac{3}{4}$ -inch gas pipe about two feet long was filled with pieces of pumice of about half the size of a pea and heated in an ordinary combustion furnace so that a length of four decimetres in the middle of the pipe were kept at a bright red heat. One of its ends was tightly connected with a flask in which benzol was kept gently boiling on a water bath. A current of carbon dioxide was allowed to pass through the benzol and with the vapor through the heated pipe. The other end of the pipe was connected with two well cooled flasks. In these the gases were condensed. The second flask carried in addition a piece of glass tube to lead away uncondensed gases into the chimney. After all of the benzol had passed through the hot iron tube, the liquid from the flasks was returned to the flask from which the benzol had been distilled and two-thirds of it were again vaporized

<sup>1</sup> J. Am. Chem. Soc., **12**, 7.

<sup>2</sup> Comptes rendus, **63**, 788, *et seq.*

<sup>3</sup> Ann. Chem. (Liebig), **174**, 201, and Ber. chem. Ges., **7**, 52.

<sup>4</sup> Ann. Chem. (Liebig), **209**, 331.

through the hot pipe. This last distillation was repeated once more. The liquids collected, containing diphenyl and unchanged benzol were united and the benzol driven off on a water bath. The residue was put into a flask with hot water, boiled, and the diphenyl distilled with steam. A good Liebig's condenser served for condensing the compound which was collected on a filter, pressed, dried and crystallized once from alcohol. Thus diphenyl was easily and abundantly obtained chemically pure and in flat, shining crystals of a snowy white.

Diphenyl, dissolved in carbon disulphide, was then treated (in the manner described in our first paper) with nitrous anhydride. The brown vapors having totally disappeared, the carbon disulphide was driven off on a water bath and the residue distilled in a current of steam, to separate the products formed from unattacked diphenyl which was condensed and regained in the cooler. The residue in the distilling flask contained an oily substance, heavier than water and but slightly soluble in it. The faintly yellow colored, watery solution was poured off and the oily mass solidified slowly. It was dissolved in alcohol.

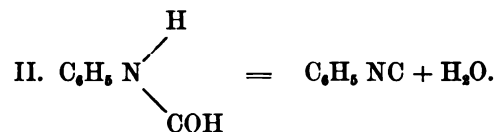
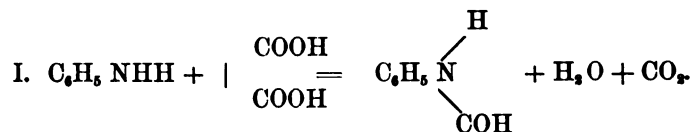
A crop of brown crystals was obtained the following day. These were redissolved in alcohol and soon deposited in long, colorless, brilliant needles which proved to be paramononitrodiphenyl of the exact melting point  $113^{\circ}$  C. The mother liquor was allowed to crystallize and deposited warty crystals, almost brick red, which as yet were not pure enough to identify. As far as our observations go, they do *not* seem to be the isomononitrodiphenyl of melting point  $37^{\circ}$  C.

*Benzonitrile and Nitrous Anhydride.*—The preparation of benzonitrile was made a special study. The methods which lead to it, are of but little practical value, except that of Krüss.<sup>5</sup> Our original intention was to follow the prescription of A. W. Hofmann,<sup>6</sup> to treat aniline with perfectly anhydrous oxalic acid. Previous experience had given us some benzonitrile in this manner, but we were astonished in this case (although working most carefully and using varied proportions) to obtain no benzonitrile *at all*, but an

<sup>5</sup> Ber. chem. Ges. 17, 1767.

<sup>6</sup> Comptes rendus, 64, 387; Ann. Chem. (Liebig) 142, 125.

abundance of phenylcarbylamine (isobenzonitrile) of offensive odor. The chemical equations for this reaction speak more simply for the result.



We, therefore, resorted to Krüss' method (*loc. cit.*), which consists in heating to 190° C. two mols. of benzoic acid with one mol. of lead sulphocyanide, well mixed in a large retort, to which a Liebig condenser is attached. Amongst other products, formed simultaneously, benzonitrile distills over, rather impure from presence of sulphur compounds. It is quite difficult to remove these latter by fractional distillation alone, but we easily obtained a product entirely free from sulphur, and boiling constantly at + 190° C., by shaking the impure oil vigorously for some time with pure metallic mercury. Benzonitrile thus prepared was used by us, and, as we shall have to repeat the reaction, will be used in future, so that the above description of its preparation will serve as a reference. The experiment did not lead to any notable reaction and we intend to repeat it, but with the difference of working in pressure tubes at high temperatures. The same will be done with diphenyl and nitrous anhydride.

*Benzaldehyde and Nitrous Anhydride.*—The product of reaction was *not* a substitution product, but the aldehyde was simply oxidized to benzoic acid. We shall consequently repeat this experiment also in sealed tubes at higher temperatures.

*Aromatic Acids and Nitrous Anhydride.*—Benzoic and phthalic acids were used. Neither of these are soluble enough in carbon disulphide to permit of an adequate reaction. A mere trifle was acted upon in both cases. The experiment was repeated, using alcohol as a solvent for the acids. The reaction was better, but

too much nitrous ether was formed and, in the case of benzoic acid, benzoic ether in addition. Substitution products formed in these reactions.

The benzoic acid, treated with carbon disulphide and nitrous anhydride, *without* using alcohol as a solvent, furnished a *nitroso* compound, the barium salt of which was prepared after we had carefully driven off the unattacked benzoic acid by persistent boiling, continued for nearly a week, replacing the water at intervals. The acid, separated from its barium salt by means of sulphuric acid, melted at 114° C. The barium salt is very sparingly soluble in alcohol, but easily in water, yielding an amber-yellow solution from which the salt crystallized in a few days. A barium determination, using 0.1949 grm. of the crystals, was made, and 0.0953 grm. barium sulphate were obtained. Theory demands 28.98 per cent. Ba for barium *nitrosobenzoate* of the formula



We found, according to the figures given : 28.73 per cent.

We have thus found a direct way of preparing nitroso acids, at least nitrosobenzoic acid, which we shall now try to obtain in larger quantities, using sealed tubes, if possible, for the reaction.

The alcoholic solution of phthalic acid, when acted upon by nitrous anhydride, furnished a yellow oil which solidified after several weeks. It could not yet be used for any determination.

COLLEGE OF THE CITY OF NEW YORK,

March 7, 1890.

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#### DETERMINATIONS OF THE FIRING POINTS OF VARIOUS EXPLOSIVES.

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BY CHARLES E. MUNROE.

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For this purpose an apparatus devised by Mr. Horsley,\* was used which consisted of an iron stand with a ring support holding a hemispherical iron vessel in which paraffine or tin was put.

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\**Trans. Soc. Eng. (Eng.)* 1872, page 15.



Above this was another movable support from which a thermometer was suspended and so adjusted that its bulb was immersed in molten material in the iron vessel. A thin copper cartridge case,  $\frac{3}{8}$  inch in diameter and  $1\frac{1}{8}$  inches long, was suspended over the bath by means of a triangle so that the end of the case was one inch below the surface of the liquid. On beginning the experiment the material in the bath was heated to just above the melting point, the thermometer was inserted in it and a minute quantity of the explosive was placed in the bottom of the cartridge case. The temperature marked by the thermometer was noted as the *initial temperature*, the cartridge case containing the explosive was inserted in the bath and the temperature quickly raised until the explosive flashed off or exploded, when the temperature marked by the thermometer was again noted as the *firing point*. The following tables contain the results thus obtained :

## GUN-COTTON.

<i>Initial temp.</i>	<i>Firing point.</i>	<i>Initial temp.</i>	<i>Firing point.</i>
65° C.	192° C.	129° C.	200° C.
65° "	201° "	148° "	200° "
80° "	198° "	156° "	199° "
90° "	186° "	158° "	199° "
125° "	199° "		

This was freshly made, compressed military gun-cotton and it was made with standard acids, viz., a mixture of three parts of  $\text{H}_2\text{SO}_4$  Sp. gr. 1.845, and one part of  $\text{HNO}_3$  Sp. gr. 1.5. One centigram. of the material was used in each of the gun-cotton experiments.

## AIR-DRIED GUN-COTTON.

<i>Initial temp.</i>	<i>Firing point.</i>	<i>Initial temp.</i>	<i>Firing point.</i>
100° C.	182° C.	170° C.	186° C.
115° "	179° "	170° "	187° "
170° "	185° "	170° "	183° "

This was gun-cotton similar to the above and made in the same way but it had been stored and transported in the wet state for about four years.

## AIR-DRIED GUN-COTTON.

<i>Initial temp.</i>	<i>Firing point.</i>	<i>Initial temp.</i>	<i>Firing point.</i>
100° C.	187.5° C.	180° C.	187° C.
160° "	186.5° "	180° "	188° "
170° "	187° "	180° "	187° "
170° "	189° "		

This was from the same source as the last but had been in the air-dried condition for probably more than one year.

## AIR-DRIED GUN-COTTON.

<i>Initial temp.</i>	<i>Firing point.</i>	<i>Initial temp.</i>	<i>Firing point.</i>
117° C.	137° C.	127° C.	139° C.
118° "	139° "	128° "	137° "
125° "	139° "	128° "	139° "

This was a freshly made, long staple military gun-cotton which had been washed as completely as possible without pulping. The acids, however, were not standard.

## AIR-DRIED GUN-COTTON.

<i>Initial temp.</i>	<i>Firing point.</i>	<i>Initial temp.</i>	<i>Firing point.</i>
80° C.	157° C.	115° C.	154° C.
90° "	154° "	130° "	155° "
100° "	154° "	140° "	158° "
110° "	156° "	150° "	161° "

This was a recently made, compressed military gun-cotton which had been made with the same acid as the last mentioned.

## DRIED GUN-COTTON.

<i>Initial temp.</i>	<i>Firing point.</i>	<i>Initial temp.</i>	<i>Firing point.</i>
80° C.	136° C.	109° C.	138° C.
105° "	142° "	119° "	141° "
108° "	137° "	123° "	136° "

This pulped military gun-cotton had been previously subjected to a temperature of 65.5° C. for some twenty minutes and then cooled. It had acquired a slight acid reaction.

## AIR-DRIED COLLODION GUN-COTTON—LONG STAPLE, SEA ISLAND.

<i>Initial temp.</i>	<i>Firing point.</i>	<i>Initial temp.</i>	<i>Firing point.</i>
121° C.	186° C.	154° C.	187° C.
123° “	191° “	159° “	186° “
125° “	189° “		

This gun-cotton was about three years old and had been stored in the dry state in a closed vessel.

## AIR-DRIED COLLODION GUN-COTTON—PULPED.

<i>Initial temp.</i>	<i>Firing point.</i>	<i>Initial temp.</i>	<i>Firing point.</i>
125° C.	197° C.	182° C.	198° C.
127° “	199° “	183° “	199° “
175° “	197° “	191° “	199° “

This was also about three years old, but had been stored wet.

## AIR-DRIED COLLODION GUN-COTTON—LONG STAPLE.

<i>Initial temp.</i>	<i>Firing point.</i>	<i>Initial temp.</i>	<i>Firing point.</i>
82° C.	193° C.	168° C.	193° C.
163° “	194° “	174° “	190° “
165° “	195° “	176° “	195° “

This was a commercial photographic gun-cotton known as “Helion” which had been stored in the dry state in a paper box, with a loose cover, for more than three years.

## AIR-DRIED GUN-COTTON.

<i>Initial temp.</i>	<i>Firing point.</i>	<i>Initial temp.</i>	<i>Firing point.</i>
120° C.	196° C.	168° C.	194° C.
167° “	197° “	169° “	192° “
167° “	194° “	171° “	194° “

This was the residue from freshly made military gun-cotton after treatment with ether-alcohol to extract all the “soluble” gun-cotton.

## AIR-DRIED GUN-COTTON.

<i>Initial temp.</i>	<i>Firing point.</i>	<i>Initial temp.</i>	<i>Firing point.</i>
127° C.	197° C.	184° C.	198° C.
171° “	197° “	185° “	194° “
184° “	198° “	188° “	199° “

This was obtained in the same way but from a sample of gun-cotton which had been stored some four years in the wet state.

## HYDRO-NITRO-CELLULOSE.

<i>Initial temp.</i>	<i>Firing point.</i>	<i>Initial temp.</i>	<i>Firing point.</i>
169° C.	201° C.	195° C.	211° C.
180° "	203° "	195° "	209° "
190° "	205° "	200° "	213° "
195° "	209° "		

This was about four years old. Had been pulped and compressed and stored in the moist state.

## NITRO-GLYCERINE.

<i>Initial temp.</i>	<i>Firing point.</i>	<i>Initial temp.</i>	<i>Firing point.</i>
150° C.	204° C.	190° C.	205° C.
180° "	203° "	190° "	205° "
185° "	204° "	195° "	205° "

This nitro-glycerine was some five years old. A single drop was taken for each experiment.

## KIESELGUHR DYNAMITE, NO. 1.

<i>Initial temp.</i>	<i>Firing point.</i>	<i>Initial temp.</i>	<i>Firing point.</i>
96° C.	197° C.	185° C.	198° C.
180° "	198° "	190° "	199° "
185° "	198° "	190° "	200° "

This dynamite was some eight years old.

## EXPLOSIVE GELATINE.

<i>Initial temp.</i>	<i>Firing point.</i>	<i>Initial temp.</i>	<i>Firing point.</i>
198° C.	205° C.	192° C.	203° C.
190° "	206° "	195° "	205° "
191° "	204° "	197° "	206° "
192° "	203° "	200° "	209° "

This explosive gelatine was freshly made.

## EXPLOSIVE GELATINE, CAMPHORATED.

<i>Initial temp.</i>	<i>Firing point.</i>	<i>Initial temp.</i>	<i>Firing point.</i>
90° C.	176° C.	140° C.	174° C.
100° "	176° "	150° "	178° "
110° "	176° "	160° "	177° "
120° "	174° "	170° "	177° "
130° "	177° "	175° "	182° "

This explosive gelatine was two years old.

## MERCURY FULMINATE.

<i>Initial temp.</i>	<i>Firing point.</i>	<i>Initial temp.</i>	<i>Firing point.</i>
130° C.	177° C.	160° C.	179° C.
140° "	177° "	167° "	175° "
155° "	179° "	170° "	181° "

This fulminate was recently made. It was wholly free from metallic mercury and was in microscopic crystals of very uniform size. The crystals were beautifully twinned and reticulated and belonged apparently to the orthorhombic system.

## GUNPOWDER—SHELL.

<i>Initial temp.</i>	<i>Firing point.</i>	<i>Initial temp.</i>	<i>Firing point.</i>
242° C.	278° C.	263° C.	279° C.
250° "	280° "	264° "	282° "
258° "	281° "	266° "	279° "
261° "	287° "		

## HILL'S PICRIC POWDER—SHELL.

<i>Initial temp.</i>	<i>Firing point.</i>	<i>Initial temp.</i>	<i>Firing point.</i>
262° C.	283° C.	271° C.	275° C.
269° "	276° "	271° "	283° "
269° "	273° "	273° "	278° "
270° "	279° "		

## HILL'S PICRIC POWDER—MUSKET.

<i>Initial temp.</i>	<i>Firing point.</i>	<i>Initial temp.</i>	<i>Firing point.</i>
238° C.	282° C.	269° C.	273° C.
239° "	290° "	275° "	285° "
240° "	285° "	280° "	288° "
244° "	289° "		

These powders had been in store about ten years and they were composed of :

Ammonium picrate	42.18
Potassium nitrate	53.79
Charcoal (best alder)	3.85

## FORCITE NO. 1.

<i>Initial temp.</i>	<i>Firing point.</i>	<i>Initial temp.</i>	<i>Firing point.</i>
60° C.	187° C.	130° C.	185° C.
80° "	184° "	145° "	190° "
90° "	185° "	170° "	188° "
100° "	190° "	180° "	190° "
110° "	191° "	190° "	200° "

## ATLAS POWDER, 75%.

<i>Initial temp.</i>	<i>Firing point.</i>	<i>Initial temp.</i>	<i>Firing point.</i>
50° C.	175° C.	140° C.	184° C.
80° "	178° "	150° "	184° "
100° "	176° "	160° "	184° "
120° "	176° "	170° "	183° "
130° "	184° "	175° "	185° "

## EMMENSITE NO. 1.

<i>Initial temp.</i>	<i>Firing point.</i>	<i>Initial temp.</i>	<i>Firing point.</i>
60° C.	178° C.	120° C.	170° C.
70° "	184° "	135° "	174° "
80° "	167° "	145° "	173° "
90° "	170° "	150° "	170° "
100° "	180° "	160° "	178° "

This emmensite had been stored in the magazine for some months in the original package (wooden box) in which it had been received.

## EMMENSITE NO. 2.

<i>Initial temp.</i>	<i>Firing point.</i>	<i>Initial temp.</i>	<i>Firing point.</i>
60° C.	177° C.	130° C.	168° C.
70° "	165° "	140° "	168° "
90° "	165° "	150° "	168° "
100° "	173° "	160° "	172° "
120° "	165° "	170° "	176° "

This was received and has been stored in a tin case.

## EMMENSITE NO. 5.

<i>Initial temp.</i>	<i>Firing point.</i>	<i>Initial temp.</i>	<i>Firing point.</i>
70° C.	205° C.	150° C.	210° C.
100° "	210° "	180° "	217° "
115° "	215° "	190° "	209° "
130° "	217° "	200° "	217° "

This was received and stored like No. 2.

## THE MANUFACTURE OF COMMERCIAL HYDROGEN DIOXIDE AND ITS APPLICATIONS.

BY A. BOURGOUNNON.

Since Bloxam, in the last edition of his "*Chemistry, Inorganic and Organic*," (London, 1888, p. 55), makes the following statement: "This compound ( $H_2O_2$ ) . . . . has no very important useful application in the arts." I have deemed it wise to state what has been and is now done in this country with this article. Bloxam's remark is perfectly true as far as pure hydrogen dioxide is concerned, but is, nevertheless, misleading. Solutions of hydrogen dioxide are now manufactured in a commercial way and chiefly applied to bleaching purposes.

My first experiments in manufacturing hydrogen dioxide were conducted in 1873 under very unfavorable circumstances; the barium dioxide which could be obtained in this city was of a very inferior quality and quoted as high as \$1.50 per ounce. I followed the method of preparation described by Thenard in 1818, and all I could produce was employed by hair dealers in their trade.

In 1878 I manufactured hydrogen dioxide on a commercial scale, and the following is a description of the method I adopted for the preparation of this bleaching compound:

The first step, and a very important one, is the hydration of the barium dioxide.

Into a suitable vessel, an ordinary cylindrical stone pot, about half full of water, the powdered dioxide is slowly poured, the mix-

ture being well stirred with a wooden spatula during this operation, and continued after its completion for about twenty minutes. Then the mixture is left alone and stirred every half hour, or oftener, for about ten minutes, until the hydration is completed. This operation requires from three to four hours; the barium dioxide forms then a thick, perfectly white and smooth, pasty mass resembling white clay mixed with water.

While the hydration is progressing a mixture of water and hydrofluoric acid is made in a vessel lined with sheet lead and surrounded with ice or simply with water in which lumps of ice are placed from time to time so as not to allow the acid mixture to rise above 10° C. during the operation.

All things being properly disposed, the hydrated barium dioxide is added in portions of three to four pounds at a time to the acid mixture, stirring all the time to mix the contents of the vessel thoroughly. All the barium is transferred to the acidulated water in about two hours and the agitation continued for four hours. If the operation has been well conducted, all the barium dioxide is transformed into fluoride, which falls to the bottom of the vessel. When this precipitate is well settled, the supernatant liquid is decanted into a vessel similar to the one used for its production, and also surrounded by ice water. The clear liquid contains an excess of acid and impurities derived from the materials employed, its color is yellowish and it must be purified to insure its keeping properties.

The impurities which are to be removed are chiefly ferric oxide, alumina and manganese oxide. To the cold solution of impure hydrogen dioxide small quantities of hydrated barium dioxide are added at a time and well stirred. When the last traces of acid are saturated, the appearance of the liquid suddenly changes, from a bright yellow it turns to a greyish color, the impurities are separated and collect at the surface of the liquid.

Without losing time the liquid is filtered through a cheese cloth stretched on a frame, and received in a vessel which contains a small quantity of sulphuric acid diluted with eight to ten times its volume of water (acid, one ounce; water, 8-10 ounces). This filtration must be quickly done. As long as the solution is alkaline



there is great danger of decomposition and loss of oxygen. If the liquid is thrown upon the filter, the latter will be quickly clogged, the filtration stopped, and the hydrogen dioxide will rapidly decompose, emitting large bubbles of oxygen with a hissing noise, but as the precipitated impurities collect first on the top of the liquid, the solution is syphoned from below these impurities, the liquid filters quickly and satisfactorily. The filtered liquid is tested for barium, and sulphuric acid is added to it until all is removed. The liquid is left over night, the precipitate of barium sulphate settles and the perfectly clear and colorless liquid is ready for the market.

All the precipitates are separated, by pressure, from the liquid they may contain, and the liquid so obtained is added to the water employed in the next operation.

I employed the following proportions:

Barium dioxide	-	-	-	-	60 pounds
Hydrofluoric acid	-	-	-	-	25 pounds
Water	-	-	-	-	40 gallons

and obtained nearly forty gallons of hydrogen dioxide. The strength of the acid was about 33 per cent.

Commercial hydrogen dioxide can be produced at the following figures:

60 lbs. Barium dioxide @ 25c.	-	-	-	\$15 00
25 lbs. Hydrofluoric acid @ 18c.	-	-	-	4 50
Ice	-	-	-	50
				<hr/> \$20 00

or fifty cents per gallon for the materials used in the manufacture. The price of 18 cents per pound for hydrofluoric acid is high.

Other methods could be employed for manufacturing hydrogen dioxide. Before adopting hydrofluoric acid I used oxalic acid, but this is not to be recommended, not only on account of the price, but because some acid may be left in the solution.

The method recommended by Thomsen consists in dissolving the barium dioxide in dilute nitric acid and when nearly all the acid is saturated, an excess of baryta water is added, hydrated barium dioxide is thrown down, is separated, washed and agitated with water containing one-third of its weight of sulphuric acid. In

this process, part of the barium can be recovered; during the treatment of the dioxide with hydrated nitric acid, a large amount of barium nitrate is separated from the liquid and this salt may be easily reconverted into barium dioxide. A stream of carbon dioxide conducted into water in which barium dioxide is added produces hydrogen dioxide, but the solution thus obtained, although very pure, is too weak for industrial applications.

The commercial solutions of hydrogen dioxide are said to contain about fifteen times their volume or useful or active oxygen. The test is made by adding to the solution sulphuric acid and potassium permanganate and measuring the volume of oxygen evolved. This method is incorrect (see my paper, this journal, June, 1889). A small amount of oxalic acid would greatly increase the volume of gas liberated.

The first application of hydrogen dioxide on a large scale in the United States was due to the experiments made in 1878 by Prof. R. Ogden Doremus in the bleaching of ostrich feathers. The process was kept secret for about a year and a half, after which it came into general use, and the manufacture of hydrogen dioxide then developed rapidly to its present extensive proportions.

Ostrich feathers are imported in bunches and are very dirty. They are strung and well washed with soap and warm water; they are afterwards rinsed until the wash water is clear and then partially dried. For the soap generally used I have substituted sodium silicate with very good results and a great saving of labor. When the feathers are clean they are immersed in the bleaching solution rendered alkaline with a slight excess of ammonia and abandoned to the action of nascent oxygen for about twelve hours, then well washed with soap or sodium silicate and warm water and rinsed, the last water containing starch, and they are beaten until dried. If one bath is not sufficient the operation is repeated. The feathers become *white*. Hair in commercial transactions is known as "human" and "Chinese." Chinese hair is bleached more extensively than human, because it is cheaper and its strength allows it to be submitted to such treatment without being too much injured. For bleaching human hair the same process is employed as for fea-

thers. For Chinese hair the first step is to render it thinner; this is done by immersions in a solution of alkaline hypochlorites, or a solution of potassium chlorate and hydrochloric acid. When the hair is "refined" it is treated like human hair; but to obtain a perfect bleaching several baths are required, sometimes as many as twelve to fifteen, and yet the white is not pure; it retains a yellowish hue which does not entirely disappear by bluing.

The very white and silky looking hair which is seen in the stores is not human; it is obtained from the yak (*Poephagus grunniens*, Linn), an animal native to the mountains of Thibet. Hydrogen dioxide is also employed to change the color of dark hair to a lighter shade. Two or three applications make the hair turn red; if continued longer a light blonde is obtained.

It might happen that some persons would have recourse to these means to conceal their identity, but it will be very easy to discover if the hair has been discolored. After about a week the newly grown hair will be darker near the roots than in their other parts.

Several other materials are bleached with hydrogen dioxide, among them wood, ivory, whalebone, silk, etc.

Tusah or wild silk is very easily bleached. It is first boiled with soap water, rinsed and transferred to the bleaching bath. I have found that a solution of hydrogen dioxide, prepared in a very rudimentary way, is all that is necessary to bleach this kind of silk.

The hydrated barium dioxide is simply dissolved in dilute hydrochloric acid, and, without removing the impurities or the barium, the solution is ready to be employed after being made alkaline with ammonia. When the silk is removed from the bath it is well washed, and to the last rinsing some hydrochloric acid is added.

When hydrogen dioxide was discovered in 1818 by Thenard, it was thought that this new compound could be advantageously employed as a medicine. Experiments carefully conducted in England failed to sustain this claim, but, nevertheless, if hydrogen dioxide is worthless as a medicine, it is a powerful antiseptic. In September, 1888, I had the opportunity of witnessing this im-

portant property. A lady suffering from cancer had had one breast amputated; at the suggestion of Prof. R. O. Doremus, hydrogen dioxide was selected as an antiseptic and the results were very favorable, the wound healed quickly without suppuration. In such cases, pure solutions must be employed; the commercial product contains free acids and when vaporized in a room produces irritation of the throat and coughing.

In conclusion, I will state that I do not believe that the manufacture of commercial hydrogen dioxide is susceptible of much development. Its chief application, the bleaching of ostrich and fancy feathers, is controlled by fashion; its use for changing the color of live hair is rapidly decreasing, henna (*Lawsonia Inermis*) which is less objectionable being a substitute. The high price of production forbids its application for the bleaching of comparatively low priced products, and unless new applications are found and the price of manufacturing greatly reduced, the demand for hydrogen dioxide cannot be increased.

Nevertheless, the preparation of hydrogen dioxide, on a comparatively large scale, is carried out in New York by the introduction of several improvements whereby as much as two hundred gallons are obtained in one operation; the stirring of the working vats is done by steam power, and the qualities of the product, which are always uniform, are highly commended and appreciated by the trade.

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## GENERAL CHEMISTRY.

### On the Presence of Nitrous Acid in the Atmosphere. L. T. LOSWAY.

In his experiments the author finds some form of combined nitrogen constantly present upon the surface of grass, leaves and branches. In clear and dry weather ammonium nitrite is converted into nitrate, either by the oxygen from the leaves or by atmospheric oxygen under the influence of sunlight. He has also found nitrous acid in the water of soils of different kinds after washing

and calcining, and then wetting with pure water. The presence of nitric acid can also be detected after destruction of the nitrous acid, but ammonia was found only in minute traces. The same soils placed in a tube and put in contact with *pure* air did not show any of the nitrogen compound substances above mentioned, even after ten days exposure. But if into the same tubes *ordinary* air was passed for twenty-six hours, the presence of nitrous acid was easily shown. (*Bull. Soc. Chim.*, [3], 2, 666.) M. L.

**Distinction of Phosphorus Oxychloride from Trichloride.** G. DENIGES.

The process is based upon the action, observed by the author, of phosphorus oxychloride on an excess of zinc powder. Flame is produced with white fumes of phosphoric anhydride. Zinc phosphide is also formed, as indicated by the production of spontaneously inflammable phosphorus hydride on addition of water to the mass.

With the trichloride there is no such action. (*Bull. Soc. Chim.*, [3], 2, 787.) M. L.

**On an Acid Cerium Sulphate.** G. WYROUBOFF.

According to the opinion of the author the question of the atomicity and atomic weight of cerium is far from settled. Mendelejeff, guided by theoretical considerations relating to the periodicity of atomic weights proposed to change the old formulæ of cerium oxides,  $\text{CeO}$  and  $\text{Ce}_2\text{O}_3$ , into  $\text{Ce}_2\text{O}_3$  and  $\text{CeO}_2$ , the atomic weight being then 141.6 instead of 94.4, the former being in accordance with the atomic heat 6.34.

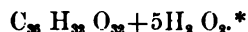
Notwithstanding this apparent accordance, the author supposes that cerium may be an exception to Dulong and Petit's law. The chemical and physical properties of the salts of cerium seem to justify the first hypothesis of the formulæ  $\text{CeO}$  and  $\text{Ce}_2\text{O}_3$ . By crystallizations of the sulphate of the lower oxide, the author has obtained the body  $\text{CeSO}_4 \cdot \text{SO}_4\text{H}_2$  with  $\text{Ce} = 94$ , a sulphate having many similarities with the sulphates of the magnesian series, being one more acid sulphate of a monoxide. If the formula were written  $(\text{SO}_3)_3\text{Ce}_2\text{O}_3 \cdot 3\text{SO}_4\text{H}_2$  with  $\text{Ce} = 141.6$ , this body would be the absolutely unique exception of an acid salt of a sesquioxide. (*Bull. Soc. Chim.*, [3], 2, 745.) M. L.

**Action of Water on Stannic Chloride.** · LEO VIGNON.

An aqueous solution of stannic chloride must be considered as a mixture of water, hydrochloric and stannic oxide. From calorimetric experiments and considerations the author concludes that the chemical state of an aqueous solution of stannic chloride is unstable, and that the modification leads towards a state of equilibrium varying with dilution and temperature. The presence of HCl retards and limits the polymerisation of the stannic oxide; NaCl and KCl do the same; this is illustrated in the use of the so called pink salt (stannic chloride and KCl) in the arts. (*Bul. Soc. Chem.*, [3], 2, 593.) M. L.

**Notes on Meilitose.** M. BERTHELOT.

This sugar was discovered by the author in 1886; rediscovered in molasses by M. Loiseau and called by him *raffinose*; found in cotton seed cake by Ritthausen, and studied by Scheibler and Tollens. The sugar obtained by Loiseau and others occurs in small crystals, containing 15.1% of water of crystallization; it corresponds to the formula



The rotary power of the solution of this hydrate is the same as that of raffinose.

Under the influence of a weak yeast ferment, only one-third of this sugar is converted, even after two weeks, although cane sugar and glucose would be entirely transformed in forty-eight hours. The probability is that this sugar breaks up into a glucose, which ferments and disappears, and a second sugar of the saccharose family able to produce a certain reduction (of Fehling solution) or a mixture of two glucoses, of which one only has reducing action. (*Bull. Soc. Chim.*, [3], 2, 655.) M. L.

**On a Nitro-Phenol: Campho-Nitrophenol, Isomeric with Nitro-Camphor.** P. CAZENEUVE.

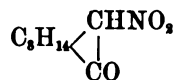
When the  $\alpha$ -nitro-camphor or the nitro-camphor, hydrochloride of the body studied by the author ([3], 1, 243) are boiled with conc. hydrochloric acid, there is obtained a neutral body, isomeric

\* The author has obtained another hydrate answering to  $C_{36}H_{72}O_{32} + 6H_2O$ .

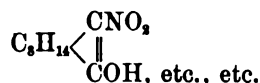
with nitro-camphor, not possessed of the acetone function, but of the tertiary or phenol function. The preparation and composition of this body are given. The formula is



It is more soluble in water than camphoric acid, soluble in all proportions in boiling water, soluble in alcohol, ether, chloroform and benzol. The author gives the crystallographic description of the crystals obtained, in dilute alcohol. In this paper, too long to be condensed, the author establishes the nature of this body. If nitro-camphor is



The new body is



(*Bull. Soc. Chim.*, [3], 1, 417.)

M. L.

#### **Fixation of Atmospheric Nitrogen by Plants. M. BERTHELOT.**

The author remarks that the belief that free nitrogen of the air takes no active part in vegetable growth is seemingly abandoned, and that this change of view has been brought about by his researches, which have shown that fixation of nitrogen is produced by the action of some kind of microbes. He cites in corroboration the experiments of G. Ville, Hellriegel and Willfarth, as to the relation of leguminous plants to this question, and those of Dehérain and Brialmont on the fixation of nitrogen by argillaceous soils. The experiments of the author have been fully confirmed by Frank of Berlin, and by Pichard and Tacke. (*Bull. Soc. Chim.*, [3], 2, 652.) M. L.

#### **Volumetric Determination of Sulphates. H. QUANTIN.**

The process is based on the insolubility of barium chromate in ammonia, and on the decomposition of a chromate by a sulphate (chromic acid being set free, and combining with the alkali of the sulphate); subsequent separation of the decomposed barium chromate by ammonia, and determination of the chromic acid by a ferrous solution, using potassium ferricyanide as an indicator. The

solutions employed are, 19.48 grms. potassium chromate in 200 c.c. water, 50–100 c.c. HCl; 24.35 grms.  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  made up to 1 litre and filtered. The solution must contain a slight excess of chromate, which must be kept account of and deducted. Indications, *modus operandi*, and examples of the accuracy of the process are given. (*Bull. Soc. Chim.*, [3], 1, 21.) M. L.

**Technical Analysis of Water.** LEO VIGNON.

The author, following the suggestion of Dr. A. Rossel of Winterthür, as to the exclusive use of sodium carbonate for the purification of waters for steam boilers, proposes a method of analysis having for its purpose to find what quantity of reagent is necessary to decompose the chlorides and sulphates of calcium and magnesium, the quantity of alkali answering to the bicarbonates having been determined once for all. This latter is calculated by the formula.

$$\frac{V \times C_v \times \text{CO}_2 \text{Na}_2}{\text{CO}_2} \times 1.9774 \text{ or } V \times C_v \times 476 \text{ grms.}$$

V, being the average quantity of water of the boiler in normal run.

V', the average quantity of water evaporated.

Cv, the volume of  $\text{CO}_2$  (in litres) for 1 cubic metre of water.

P, the quantity of  $\text{Na}_2\text{CO}_3$  answering to sulphates and chlorides.

P V', the quantity of reagent to be used daily.

The process is volumetric and takes : 1st, a solution of calcium hydrate ; 1gr.80 per litre ; 2d, alcoholic phenolphthaleine ; 3d, a solution of  $\text{CaCl}_2$ , 5 per cent. strong ;  $\text{Na}_2\text{CO}_3$ , 1 grm. per litre, etc. (*Bul. Soc. Chim.*, [3], 2, 596.) M. L.

**Detection of Free Chlorine in HCl.** G. A. LEROY.

Very small traces of Cl can be detected by addition of a few crystals of diphenylamine to the acid. (*Bul. Soc. Chim.*, [3], 2, 789.) M. L.



## ABSTRACTS.

### Abstracts of American Patents Relating to Chemistry.

(From the U. S. Patent Office Gazette.)

Issued February 25th, 1890.

**421,904.**—Process of bleaching wax. W. Bruening.

The wax is atomized by a jet of steam or air, and the resulting powder bleached by the action of light, air and moisture.

**421,985.**—Process of making alkaline salts of antimony. J. Holliday.

The alkaline antimonites, generally considered antimonoso-antimonates, are prepared by treating metallic antimony in hot solutions of an alkaline nitrate or nitrite and caustic alkali.

**422,018.**—Blue-green dye. A. Herrmann.

Derivative of metaoxytetraalkyldiamidotriphenylmethane.

**422,118.**—Process of carburizing malleable cast iron or low carbon steel. M. F. Coomes and A. W. Hyde.

The metal, raised to a white heat, is placed in a bath composed of water or milk and a carbohydrate.

**422,119.**—Process of carburizing malleable cast iron or low carbon steel. M. F. Coomes and A. W. Hyde.

The metal, raised to a white heat, is immersed in milk.

**422,120.**—Process of carburizing malleable cast iron or low carbon steel. M. F. Coomes and A. W. Hyde.

The metal, raised to a white heat, is placed into a bath containing an organic acid, which results from the oxidation of glycogen.

**422,121.**—Process of carburizing malleable cast iron or low carbon steel. M. F. Coomes and A. W. Hyde.

The metal, raised to a white heat, is placed into a bath formed by adding to water or milk a mixture of a carbohydrate and an oxidizing agent.

**422,128.**—Furniture polish. J. M. Hall, C. Morris and W. S. Hamilton. Consists of Japan drier, linseed oil, turpentine, copal varnish, alcohol, hydrochloric acid and olive oil.

**422,140.**—Process of recovering alkali and glycerine from spent soap lye. E. D. Mellen.

The soap is precipitated from the soap stock by an excess of aqueous

solution of alkali, whereby the resulting lye is obtained free from salt, after which the lye is concentrated and saturated with carbon dioxide, which separates the alkali as bicarbonate and leaves the glycerin in solution.

**422,141.**—Apparatus for making soap and carbonic acid. E. D. Mellen.

**422,178.**—Gas washer. F. A. M. Alavoine.

**422,195.**—Varnish. W. D. Field.

A non-hygroscopic varnish or lacquer for use on metals and hard or non-absorptive surfaces, consisting of a concentrated solution of shellac, in combination with a solution of pyroxylin in a practically non-hygroscopic menstrum miscible with the shellac solution.

**422,284.**—Condenser with multiple effect evaporator. S. M. Lillie.

**422,285.**—Evaporating apparatus. S. M. Lillie.

**422,322.**—Carburetor. J. W. Strouse and A. B. Strouse.

**422,334.**—Hydrazin. T. Curtius.

**422,357.**—Filter. F. T. Weidan and W. E. Kane.

*Issued March 4th, 1890.*

**422,369.**—Drum for fluid-separating machines. W. Bergh.

**422,408.**—Process of making steel containing carbon, manganese and aluminium. R. A. Hadfield.

**422,480.**—Printing ink. J. McCloskey and C. F. Farwell.

An ink for printing upon celluloid, consisting of pigment, albumin (animal or vegetable) and glycerin.

**422,464.**—Baking powder. H. D. Thatcher.

Consists of cream of tartar, an alkaline bicarbonate, and sugar of milk.

**422,484.**—Adjustable filtering and percolating stand. A. P. Yarnall.

**422,500.**—Process of purifying aluminium chloride. H. Y. Castner.

Iron is removed from aluminium chloride by melting the crude chloride and treating it electrolytically.

**422,509.**—Process of obtaining chromium and chromium alloys. A. K. Eaton.

Consists in first producing a chromite of the desired metal, and then reducing the chromite to an alloy.

**422,514.**—Manufacture of explosives. S. H. Emmens.

Consists in fusing a suitable hydrocarbon substitution derivative, such as trinitrophenol, adding a suitable nitrate, continuing a sufficient degree of heat until actual liquefaction of the mixture is attained, and then allowing the same to cool.

**422,515.**—Manufacture of explosives. S. H. Emmens.

**422,692.**—Apparatus for the manufacture of gas. J. D. Averell.

**422,750.**—Polishing powder. E. P. Eells.

Consists of callustro, ammonium carbonate, and sodium carbonate.

**422,806.**—Apparatus for distilling wood. O. Koch.

*Issued March 11th, 1890.*

**422,907.**—Artificial fuel. J. Bowing.

Coal and coke dust, breeze, and similar substances are agitated with tar or pitch, in or under water, and allowed to settle. The water is then drawn off, and the mixture formed into blocks or briquettes, and dried.

**422,989.**—Method of separating impurities from salt. T. Higgin.

**423,011.**—Hydrocarbon burner. J. Wilson and A. Mason.

**423,012.**—Process of burning petroleum or other hydrocarbons. J. Wilson and A. Mason.

Consists in injecting oil, steam and air into a highly heated retort, and discharging the resultant products at the burning point.

**423,042.**—Waterproof composition for roofing, etc. A. M. Ford.

Consists of steam, pitch, oil, soap and petroleum.

**423,044.**—Apparatus for the manufacture of oil gas. W. B. Frink.

**423,047.**—Paint. W. B. Grover.

Consists of rubber pulp dissolved in dead oil of coal tar, a drier, a varnish, a mineral coloring matter, and the distilled unbroken residuum of bituminous gas coal tar.

**423,071.**—Production of restored or devulcanized rubber. N. C. Mitchell.

Consists in devulcanizing the rubber by the action of live steam, then while the rubber is yet moist rolling it until reduced to a powder, and finally drying the powder, and at the same time agitating or keeping it in motion to preserve the powdery condition.

**423,101.**—Process of electroplating non-metallic articles. W. H. Winslow.

**323,127.**—Apparatus for making infusions. J. Childs.

**423,181.**—Hydrocarbon injector burner. C. Cole.

**423,183.**—Cooling and refrigerating apparatus. H. J. W. S. Cooke.

**423,188.**—Weighing scales. J. G. Schmidt.

**423,213.**—Obtaining peptone and maltose. A. Brunn.

Albuminous and starchy substances are converted into peptone and maltose by fermentation, after which the peptone and maltose are separated by lixiviation with water.

**423,230.**—Explosive. S. H. Emmens.

Consists of paper or paper stock converted into a nitrocompound and impregnated with ammonia and picric acid.

**428,257.**—Carburetor. L. C. Huber.

**428,268.**—Making malted bread. J. Montgomerie.

Consists in first mixing flour, water and extract of malt or maltine, heating the mixture in a water bath to 130°–150° F., with agitation, maintaining it at that temperature for a few hours until the diastase acts on the starch and converts it into soluble dextrin and sugar, then making a dough of this compound by further addition of flour, and subsequently forming and baking the same.

**428,281.**—Alloy. W. V. Shelton.

Composed of copper, zinc, nickel, iron, manganese and silicon.

**428,306.**—Apparatus for the manufacture of ice. J. W. Brook.

**428,320.**—Process of making phosphatic fertilizers. E. R. Hodgkins.

Consists in combining finely pulverized phosphatic material and calcic oxide, slaking the calcic oxide by the addition of water, and finally intimately mixing the ingredients.

**428,341.**—Green dye. A. F. Poirrier.

Green or greenish coloring matters are produced by condensing with tetramethyldiamidobenzhydrol, in a hydrochloric or sulphuric acid medium, paratoluidine, a metaxylidine, pseudocumidine, amidotrimethylbenzol, or mesidine, and subjecting the leuco bases thus formed to oxidation, or oxidation in conjunction with the formation of hydroxyl, methyl, ethyl, benzyl and sulpho-conjugated benzyl derivatives of said leuco bases.

**428,347.**—Apparatus for generating and burning gaseous fuel in furnaces. E. P. Shetter. W. R.



REGULAR MEETING, April 4th, 1890.

Vice-President Breneman in the chair.

Dr. C. E. Munsell was appointed Recording Secretary, *pro tem*.

Mr. E. J. Milhau, 183 Broadway, New York, was elected an associate.

The following nominations were read : Ernest J. Lederle, Ph. B., P. O. Box 197, Stapleton, Richmond Co., New York, as a member ; Dr. William McMurtrie, N. Y. Tartar Co., 63 William street, New York, as a member ; Lt. W. R. Quinan, Supt. California Powder Works, Pinola P. O., California, as an associate member.

The following papers were read :

On the preparation of thiophene (with exhibit and experiments),  
by L. H. Friedburg, Ph. D.

Titanium in Blast Furnaces, by Auguste J. Rossi, Ph. D.

The meeting was then adjourned.

C. E. MUNSELL,  
Recording Secretary, *pro tem*.

## THE KEKULÉ ANNIVERSARY.

The celebration by the Berlin Chemical Society, of the twenty-fifth anniversary of the announcement of the benzol theory and the reception to its author Prof. August Kekulé, occurred at Berlin, on March 11, 1890.

Notices of the coming celebration were received by the American Chemical Society, with an invitation to send a representative to the meeting, but the time was too short to permit of action by the Society. Official acknowledgment of the invitation was made, however, in the following letter by the president, Prof. H. B. Nason.

TROY, N. Y., Feb. 22d, 1890.

TO THE PRES'T OF THE CHEM. SOC. OF BERLIN :

*My Dear Sir :* Your kind letter inviting us to send a representative to the Kekulé Festival on the 11th of March is at hand. We regret exceedingly that we cannot be represented there, but desire to express our deep interest in the Festival, as well as in the man who has done so much for the advancement of Chemistry.

Believe me, my dear sir, to remain, yours most truly,

H. B. NASON,

Pres't of the "Amer. Chem. Society."

Adequate accounts of the meeting through scientific sources have not yet reached this country. The following extract from a daily paper of Berlin will be of interest:

*(From the "Vossische Zeitung," March 12, 1890.)*

The great celebration given yesterday by the German Chemical Society, in the large room of the City Hall, in honor of August Kekulé, upon the twenty-fifth anniversary of the formulation of the benzol theory was a reunion of the representatives of chemical science from every quarter.

By the side of the honored guest, whose seat was entwined with foliage, was seated the representative of the government, Minister

of State von Gossler. Among others present were the Director General of the Royal Museum, Privy Counsellor Schoene; the Director of the Museum of Natural History, Privy Counsellor Moebius; the Director of the Imperial Board of Health, Privy Counsellor Köhler, in company with "Regierungsrath" Prof. Sell; the Director of the Bureau of Statistics, Privy Counsellor Blenk; the Rector of the Technical High School, Prof. Jacobsthal; the President of the Photographic Society, Prof. Vogel; the Aldermen Marggraf and Borchardt and others.

Of the numerous chemists who appeared, some of them even from the New World, were Prof. Armstrong of London, Prof. Körner of Milan, Prof. Bischof of Riga, Profs. Wislicenus of Leipzig, von Baeyer of Munich, Victor Meyer of Heidelberg, and his brother Rich. Meyer, Poleck and Ladenburg of Breslau, Zincke of Marburg, Döbner and Volhard of Halle, Wallach of Göttingen. Privy Counsellor Dubois-Reymond represented the Academy of Sciences. Practical chemistry also was represented by the bearers of well known names; we mention only Directors Finkelberg and Holtz of Schering's Works, and Hasenclever of the Rhenania, Dr. Bannow of the firm of Kahlbaum, Dr. Sarnow, Dr. Kraemer, Dr. Marrasse and others. The spaces under the arcades were occupied by ladies.

Prof. von Hofmann, as President of the German Chemical Society, opened the meeting with words of welcome and presented a letter from the Cabinet of the Emperor in regard to the celebration, which had been "noticed with especial interest; returning thanks for the invitation and regretting that it was impossible to be present." Prof. Hofmann then briefly described the origin of the benzol theory and gave a sketch of its importance to science and industry. He showed in a striking manner how a small thought may permeate an entire science, and how Kekulé's theory in particular will be a guiding star towards which chemical investigators of coming generations will thankfully direct their eyes.

Dr. Adolph von Baeyer of Munich, the successor of Liebig and the oldest of Kekulé's pupils, commended the work of Kekulé in the light of the latest investigations, and characterized the



celebration as the crowning festival (Richtfest) of structural chemistry.

Prof. Wichelhaus congratulated the honored guest of the meeting in the name of the German Chemical Society, and presented an address artistically executed by K. Roehlich.

Prof. Armstrong, representing English chemists, offered an address printed in gold upon white satin, the reading of which was received with great applause. The address of the French chemists was read by Prof. Martius. Prof. Bischof spoke for the chemists and physicists of the Russian Empire, and characterized the celebration as a day of triumph for science. He also presented an address, which was heartily applauded. Prof. Durand Woodman, of New York, spoke in English for the chemists of America.\* Prof. Körner, of Milan, a former assistant of Kekulé, spoke for the chemists of Italy, and especially for the academies and universities. The Academie de Lincei of Rome and numerous corporations of Italy also sent congratulations. For the industry of the coal tar colors Dr. Glaser, of Ludwigshafen, delivered a lengthy address, and announced the completion of a portrait of Kekulé by Prof. von Angeli, which was to be presented after the dinner, and which is to be hung in an appropriate place in this city.

Prof. Kekulé, in conclusion, heartily thanked the assemblage for the ovations tendered him, which he declared to be "far above his deserving." His remarks, which were as modest as they were witty, were enthusiastically received by the meeting.

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\* Dr. Woodman was in Berlin at the time of the celebration, and, at the request of Prof. A. W. Hofmann, and as a member of the American Chemical Society, merely read the letter of the President of the Society, Prof. Nason, which is published herewith. In a letter to the editor he disclaims any attempt to act as the official representative of the Society or of the chemists of America in the absence of direct authority to do so.

## ON THE PREPARATION OF THIOPHENE.

BY L. H. FRIEDBURG, PH. D.

Pursuing the investigation in regard to the formation of anthraquinone from thiophenalddehyde<sup>1</sup> it was found that thiophene could be prepared at about one-fifth of the price of the imported article (nearly forty dollars per pound), and it was therefore made in the laboratory.

Although the preparation of thiophene is not new<sup>2</sup>, nor especially difficult, it may be useful to others to have a description of the method in detail.

The preparation of thiophene involves the use of sodium succinate and phosphorus trisulphide. Thiophene is produced when these two substances are jointly subjected to destructive distillation.

*Sodium Succinate.*—Succinic acid is more easily obtainable than its salts. In each case 450 grms. of succinic acid (about one pound) were dissolved in a litre of boiling distilled water. The acid used was the intermediate one of the three kinds offered in the market, called "pure." It was clean, white and of very nearly the correct melting point, between 178° C. and 185° C. It is sufficiently pure for our purpose. The gently boiling solution was very gradually saturated with the so-called dry sodium carbonate. This latter is *not* dry, *nor* pure, but loses, when fused, 31.66 per cent., which loss is due to water and also to carbon dioxide, bicarbonate being present. It does *not* contain ammonium salts, as proved by Nessler's test. 600 grms. of such sodium carbonate, finely powdered, were used.

After neutralization, the liquid was allowed to stand over night. About 800 grms. of well formed, colorless crystals of sodium suc-

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<sup>1</sup> J. Am. Chem. Soc., 12, 26.

<sup>2</sup> Ber., 18, 454.

ciate were obtained the following morning. The mother liquor was poured off and evaporated on the water bath, stirring towards the end of the process. The resulting mass was more yellow than the crystals first obtained. The crystals were allowed to drain in a large funnel on a tuft of glass wool, a small cylinder of wrapping paper being inserted in the tube of the funnel. Both crops were then dried in a steam oven. The crystals offer no difficulty in drying, but the evaporated mass must be put into a dish, because it liquifies partly during the first hours of drying. After two days treatment in this way all of the salt was spread upon filter paper and put into a drying oven kept constantly at about  $110^{\circ}\text{C}$ . Continuing this treatment for a week, the six mols. of water, with which sodium succinate crystallizes, were finally expelled. The mass does not powder very easily and spreads an irritating dust. It is passed through a sixty mesh sieve and kept in well-stoppered bottles.

*Phosphorus Trisulphide.*—This mixture, which, as a dehydrating agent we owe to Kekulé, was prepared in the following manner. Absolutely dry red phosphorus, and dry washed flowers of sulphur were most intimately mixed in the proportion of 62 P to 96 S, first on a large sheet of paper with a broad spatula, crushing every small lump of phosphorus which might remain, then in a mortar. The mixture has to be fused together. Since I prepared  $2\frac{1}{2}$  kilos. of it in a very short time, with little loss of material, I will give the mode of procedure.

Take two sound Berlin porcelain crucibles, 2 in. deep,  $3\frac{1}{2}$  in. upper and  $1\frac{1}{2}$  in. lower diameter, with covers. Put each into an iron ring on a tripod, so that the ring clasps the crucible at about two-thirds of its height. Work under a good hood to carry off vapors. With a porcelain spatula, nearly as broad as the mouth of the crucible, put as much as the spatula will comfortably hold into the crucible. Cover and heat gently with a Bunsen burner. A slight explosion is heard, a faint flame becomes visible through the translucent crucible and white vapors are forced out at the edge of the cover. Remove the burner; it is unnecessary to heat the crucible further. The next charge is added as soon as no spontaneous combustion occurs on lifting the cover of the crucible.

Gradually and in small portions, as indicated, the crucibles are filled, finally almost to the edge, with the quietly flowing molten mass. The covers must not be opened unnecessarily. The crucibles are allowed to cool. When quite cool they are tilted over a clean piece of paper and a gentle tap brings out the cone. The mass is crystalline in part, waxy and of a dark grayish yellow. It is broken into large pieces and these are at once transferred to quite dry, wide salt-mouthed bottles and the stoppers are sealed with paraffine.

The loss of material by burning, if the process is carried out as above, is slight, being between six and eight per cent. I obtained, for instance, from a charge consisting of 124 grms. of phosphorus and 192 grms. of sulphur, 298 grms. of the so-called phosphorus trisulphide, thus having lost but 18 grms. The average charge for *two* crucibles of the size mentioned is a little greater. Most of the loss involved occurs at the beginning of the operation, when the crucibles are then only partly filled and air is more abundant within them than afterwards.

*Thiophene.*<sup>1</sup>—The process of destructive distillation of sodium succinate with phosphorus trisulphide was carried out in a tubulated, two litre retort, higher than broad, connected with a Liebig's condenser, four feet long. A smaller cooler may do as well or even a well cooled flask, into which the neck of the retort reaches, might serve, but a long condensing tube retains more of a semi-solid yellow substance, which is also formed in this process, and thus the distillate obtained is purer.

Not more than about 155 grms. of sodium succinate are weighed out and mixed intimately with the double quantity, viz., 310 grms. of well crushed phosphorus trisulphide. The powdering of the trisulphide is facilitated by adding a little of the dry succinate powder from the start. The mixture is run, by means of a wide funnel, into the retort, which it nearly half fills. The bottom of the retort rests free in a ring, *without* either wire gauze or iron plate underneath it.

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<sup>1</sup> J. Am. Chem. Soc., 12, 29, foot note.

By means of the full flame of a broad round burner a uniform heat is applied. The mass soon begins to assume a dark brown color in spots. The burner is removed and the reaction continues. The mass swells a little, vapors which contain much hydrogen sulphide are given off, so that most perfect ventilation is necessary during the process. Soon the neck of the retort and the condenser tube become lined with yellow drops, condensing in the cooler to a half solid substance, while an abundant flow of an almost colorless liquid fills the receiving flask. After some time (generally in about ten minutes) the distillate runs less briskly. Then the heat under the retort is renewed, until the dropping becomes so slow as to make further work unprofitable.

The distillate, which has a golden yellow color, is at once redistilled from a water bath, yielding an easy flowing, almost colorless oil, still slightly impure from presence of  $\text{H}_2\text{S}$ .

I remark here, that it is more profitable *not* to distill such a small quantity as we obtain from 155 grms. of sodium succinate, but to repeat the process, just described, four times with little or no interruption with new quantities of mixture, in new retorts and then to redistill the united crude distillates. All this can be done in two hours.

The redistilled oil is then shaken with dilute alkali, which turns brown, while the oil (which, according to the strength of the alkali used, floats upon it or sinks below it) assumes its purer, colorless appearance. The two liquids are separated, either by a syphon or by a separating funnel, this latter being better for vigorous shaking and subsequent washing of the oil. The thiophene obtained, being but slightly opalescent from water retained in it, is filtered through a small, dry, fluted filter into a flask with good stopper.<sup>1</sup> Some long, thin strips of clean sodium, showing metallic lustre, are put into the thiophene and the liquid is allowed to stand with the metal over night. Then the thiophene

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<sup>1</sup> A previous shaking with calcium chloride is *not* necessary, nor is it advisable. In one instance, when I tried to dry the oil with a little solid, very pure  $\text{CaCl}_2$ , a faintly rose colored solid was formed at the expense of the oil, and I had to dissolve in water and distill again.

is distilled from the sodium on a water bath. It is thus perfectly pure. The sodium assumes the color of "old gold."

From nearly 610 grms. of sodium succinate and 1,200 grms. of phosphorus trisulphide, treated in the manner described above, I obtained 150 grms. of pure thiophene. This is the obtainable yield, it is almost fifty per cent. of that indicated theoretically :



At first I worked with quantities of sodium succinate up to 200 grms. and more at a time. I also purified each raw distillate as soon as obtained, but got only 100 grms. of pure thiophene from 600 grms. of succinate. Most of this discrepancy I have to attribute to the visible loss by adhesion of drops of oil to the wash liquids and in the distilling flasks ; some of it, of course, also to the large quantities used for destructive distillation. I therefore recommend most strongly to use the figures given in my directions.

The yellow substance, semi-solid in the cooler (some of it had also run down into the receiver), was allowed to drop slowly into a dish. It continued for days to give off  $\text{H}_2 \text{S}$ , and when put into a tube, closed by a cork, was puffed up towards the latter ; it gradually became harder, however. The black, uniformly caked mass in the original retort can be used to advantage for the preparation of hydrogen sulphide, this latter being developed from it by the addition of water. If, after the development of  $\text{H}_2 \text{S}$ , the mass is filtered, leached with water and the extracts filtered, the liquids evaporated to almost a syrup (which process gives rise to a new evolution of  $\text{H}_2 \text{S}$ ), then put over a dessicator, white crystalline crusts begin to deposit and more  $\text{H}_2 \text{S}$  is given off. The liquid is of acid reaction. With reagents it answers neither to the phosphoric acid, nor to the sodium sulphide tests,<sup>1</sup> but acts in general as a strongly reducing substance, indicative of *phosphorous* acid. The following reactions, which were performed with it, speak for themselves :

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<sup>1</sup> J. Am. Chem., Soc., 12, 29 ; foot note.

*Neutral lead acetate*: White ppt., not changed on boiling.

*Alkaline sol. of lead acetate*: White ppt., not changed on boiling.

*Acetic acid sol. of lead acetate*: White ppt., not changed on boiling.

*Silver nitrate*: Yellow ppt., turning brown and ultimately black on boiling.

*Mercuric chloride*: White ppt., heavy gray on boiling.

*Mercurous nitrate*: White, brown, finally black ppt.

*Cupric sulphate*: Green ppt., on boiling reduced to red oxide and even to metallic copper.

*Ammoniacal sol. of  $\text{Cu SO}_4$* : Blue ppt., green on boiling.

*Ammoniacal sol. of  $\text{Ag NO}_3$* : Brown ppt., then black and reduced to silver.

*Ammonium molybdate*: No precipitate, the liquid turned blue, indicating reduction to molybdic oxide. The same reaction took place when the liquid tested was previously neutralized with  $\text{Na}_2\text{CO}_3$ .

*Barium chloride*: No precipitate.

*Ferric chloride*: Acid and neutral, white ppt., unchanged on boiling.

*Magnesium sulphate* (after  $\text{N H}_4\text{Cl}$  and  $\text{N H}_4\text{OH}$ ): white ppt. cold or boiling.

*Ammoniacal Ammonium molybdate*: also reduced to clear blue liquid.

*Platinic chloride*: nothing, cold, on heating the liquid turned mahogany brown and a black precipitate formed.

*Potassium iodide*: no ppt., no coloration, cold or hot.

*Iodic acid*: abundant reduction to iodine.

*Potassium permanganate* (neutral): strongly reduced, first with simple decoloration. On adding more, until distinctly red and then boiling, chocolate brown precipitate.

*Sodium hydrate* (saturated sol.): black ppt.

*Nitric acid* (conc.): Flocks of sulphur separate on boiling. The liquid filtered off did not give a ppt. with ammonium molybdate.

*Conc.  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$*  produced opalescence and evolution of  $\text{H}_2\text{S}$ .

When the original salt solution was evaporated to dryness in a porcelain crucible, spontaneously inflammable hydrogen phos-

phide was evolved in abundance. Finally the mass turned black and fused to a black, translucent glass. At the end of a platinum wire in a Bunsen flame (outer or inner) the glass swelled and gave a clear colorless bead. This, dissolved in water, did *not* yield a ppt. with molybdate solution.

I cannot decide, as yet, whether the liquid giving the above tests is the solution of a uniform salt, or whether it contains several salts, and if so, what may be the nature of these. It is very apparent, however, that *phosphorous* acid, or phosphites, or both, are present in it. The formation of these is easily explained, if we consider the substances present in the retort in which destructive distillation of sodium succinate with  $P_2S_3$  was taking place, after the formation of thiophene had begun. The probability that a phosphoric acid, containing sulphur for some of its oxygen atoms, may have formed, is also indicated.

This salt mixture, which doubtless retains some sodium sulphide, invites future study. (J. Am. Chem. Soc. 12, 29, footnote.)

On redistilling the first *crude* oil from the waterbath, a considerable amount of an oil, non-volatile at steam heat, remained, together with a yellow solid substance. This oil, of peculiar odor, faintly amber colored, did not permit of fractional distillation at once. It amounted to about 25 c. c. At  $87^\circ$  C. it began to boil and gave some distillate, evidently containing thiophene. The temperature rose soon to  $95^\circ$  and then more rapidly to  $120^\circ$  C. Then suddenly a large amount of gas was given off. This effervescence subsided and gave way to a quiet flow of the liquid, which meanwhile had assumed a dark brown color. Finally, and almost instantaneously, the temperature rose to  $220^\circ$  C. and the mass was driven up into the neck of the retort. The distillate was treated several times with solution of alkali, then washed, dried with a pinch of fused sodium chloride, filtered, shaken with metallic sodium and distilled from the same. I fractioned out of it six c. c. of an oil which gave the indophenin reaction and boiled at  $86^\circ$  to  $99^\circ$  C.

In regard to the properties of thiophene I refer to my paper on anthraquinone<sup>1</sup>. In addition, it may be remarked that the

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<sup>1</sup> J. Am. Chem. Soc., 12, 26 *et seq.*



specific gravity of thiophene, at 23° C. is 1.062. For this and other particulars see "Die Thiophen Gruppe."<sup>1</sup>

The two most characteristic reactions of thiophene being the indophenin and the phenanthraquinone reactions, care should be taken to use pure isatin and pure phenanthraquinone.

The brown commercial isatin is not fit to be used for the purpose. It is very simply purified by dissolving in a solution of potassium hydrate and then carefully adding hydrochloric acid, drop by drop. A leather-brown precipitate is formed, which is filtered at once. The filtrate, on addition of a little more H Cl, yields a bright brick-red or vermilion precipitate of pure isatin. A drop of thiophene is mixed with ten c. c. of pure benzol. *Very* little isatin is introduced into this mixture and then conc. H<sub>2</sub> S O<sub>4</sub> is slowly run into the same, shaking the test tube all the time. The mixture assumes a deep color, more green than blue. On addition of water, indophenin is precipitated in dark blue flocks. These are soluble with marine-blue color in chloroform, the solution showing its tint also by gaslight.

The phenanthraquinone is obtained from commercial phenanthrene, which can be bought quite pure and of the correct melting point, 99° C.

21 grms. of such phenanthrene are oxidized in a mixture of :

30 grms. potassium dichromate,  
15 " conc. H<sub>2</sub> S O<sub>4</sub>,  
54 " water,

according to Fittig and Ostermeyer<sup>2</sup>. These authors recommend a recrystallization from equal volumes of glacial acetic acid and water. The phenanthroquinone thus obtained crystallizes in remarkably pretty tufts of gold bronze lustre<sup>3</sup>.

College of the City of New York. April 3, 1890.

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<sup>1</sup> Pages 20 *et seq.*

<sup>2</sup> Ann. Chem. (Liebig), **166**, 361; see also **196**, 38.

<sup>3</sup> For the reaction between thiophene and phenanthraquinone, see J. Am. Chem. Soc., **12**, 30.

## TITANIUM IN BLAST FURNACES.

BY AUGUSTE J. ROSSI.

The influence of titanium or titanitic acid on the fusibility of the slags and upon the regular working of the blast furnace is a question upon which we have had but very few direct investigations in this country and in which, to the enlightened practice of Europe, has been opposed a kind of prejudice, possibly justified in certain circumstances but not based on well defined or precise grounds, and frequently in contradiction with the facts.

Phosphorus has certainly an injurious effect on iron and cast iron, but for many purposes to which the latter is applied phosphorus pig is much in demand for fine castings not requiring great strength, and, although in general it is an element to be avoided in an iron ore, the question is one of relative quantities admissible for certain purposes. But while as to phosphorus the subject has been exhausted, so that we know with certainty between what limits we can use phosphorus ores with advantage, the same cannot be said of titanium.

The question may be stated as follows : Is titanium an element so obnoxious that ores, otherwise excellent, easily and cheaply obtained, should be rejected on account of its presence, even in small or limited quantities? Is it the excess of this element which has caused this general prejudice, and is the latter justifiable in all cases? Are there any limits within which the presence of titanium would pass unobserved and would not influence the working of the furnace?

We have endeavored in this paper to throw some light on these points by presenting the facts collected upon the subject in the course of certain researches that we have been called upon to make. We shall give, in a condensed form, the literature of titan-

ium, satisfied if we can contribute in some measure the elements of a conscientious investigation, independent of any personal or preconceived opinion.

That a prejudice may have existed for a long time without any apparent reason is strikingly illustrated in the practice of the blast furnace. For many years lime alone has been considered as the only real fluxing element in a limestone. Calcites, often more difficult or more expensive to obtain, have been exclusively used as fluxes, while dolomites, near at hand and cheaper, have been rejected under the impression that magnesia had no fluxing properties. If such an impression arose from the fact that magnesium silicate is infusible, the same could have been said with equal truth of aluminium silicate, and still aluminous ores have been always considered as very advantageous in the blast furnace. But the same objection would apply to lime, for of all the compounds that silica can form with lime *alone*, only one is practically fusible in the blast furnace. Lime in excess in a slag will render it so infusible and so pasty as to be the cause of grave disorders, "filling up the hearth with infusible blocks, which, in some cases, have been found to weigh as much as 30 tons. Will it be said that lime has no fluxing properties? The fact is that the double silicates of lime and magnesia or of alumina and magnesia are enormously more fusible than the simple silicates of these bases and *as fusible* or even more so than the corresponding silicates of lime and alumina which for years have constituted the slags of many furnaces exclusively. The introduction of a third base into a double silicate will considerably increase its fusibility, triple silicates fusing much more readily than double silicates. Beside, as far as saturation of silica is concerned, one pound of magnesia, to form a silicate of a certain character, a neutral silicate, for instance, will take up  $1\frac{1}{2}$  pounds of silica, while lime will take up only 1.07 lbs. Hence with a dolomite as a flux, with ores containing a certain quantity of alumina, as they almost invariably do, there will be not only a saving on the first cost, but the quantity of limestone necessary will be decreased, the amount of foreign matters to be fused diminished and the fusibility of the slag increased. It is only at a comparatively recent date, however, that iron masters have recognized these

facts, and such an authority in metallurgy as Dr. Percy stated in 1864 that "*The use of dolomite as flux instead of calcite must be avoided; it tends to produce infusibility of the slag*" (Percy's Metallurgy, p. 506).

Titanic acid is a substance very tedious and difficult to determine in iron ores and pig irons, as every chemist knows. Sometimes, according to the state in which it is present in the ores, it may be precipitated with the insoluble residue of silica obtained from the fluxing of the ores with alkaline carbonates and nitrates and subsequent treatment, and it may then be mistaken for silica. Although it imparts to the latter a yellowish coloration when ignited, this coloration disappears by cooling and it may be overlooked, or, when titanic acid is present in small quantities, the coloration may not be noticed. It may and will generally pass into the acid solution obtained from the filtration of the insoluble residue and there, occasionally, may show its presence by causing the filtrate to run milky when the precipitate on the filter is washed with water. Frequently these indications are lacking and, if not specially determined by approved methods, titanic acid will be overlooked and mistaken for iron, to which it "sticks," as Mr. Riley says (Journal of British Iron and Steel Institute). It will vitiate the determination of phosphorus, in many cases absolutely preventing the precipitation of phosphoric acid.

(See for determination of titanium in iron ores, pigs and steel, the excellent papers of Messrs. Shirmer, Drown and others, American Institute of Mining Engineers; A. A. Blair's Analysis of Iron, Tenth Census of the U. S., Vol. XV., 1880.)

#### *Literature of Titanium.*

Titanium is an element found almost everywhere. It is present in variable quantities in many rocks, ores and minerals. Magnetic ores frequently contain titanic acid, and thus titanium finds its way into many blast furnace slags and into pig irons. It is met with in trap, basalt, mica, gneiss, garnet, amphibole, hornblende, etc., hence in many clays and certain mineral waters. It has been detected in meteorites and is an important constituent of the solar atmosphere (Roscoe & Schorlemmer's Chemistry, p. 255), its pres-

ence being indicated by certain dark bands in the ultra violet spectrum (Watts' Dictionary of Chemistry, 1872, p. 1976) ; it is found in nearly all crystalline rocks, hematites and magnetites (Bauerman's Metallurgy, p. 53, etc.).

Titanic acid is found in comparatively large quantities in the ash of coal. Very many samples of coal from widely separated districts gave it in every instance (Chemical News, 1883, p. 157), in some cases as much as 0.16% of the ash. It is also found in limestones in small quantities, and in fact in all the materials that enter a blast furnace. It is found in many iron ores and clays, and generally in silicates, consequently also in blast furnace slags (Fresenius Quantitative Analysis, p. 127). Chemically, titanium is closely related to tin ; it used to be described as a rare element, but it has been found lately to exist in considerable quantities in iron ores and clays (Bloxham's Chemistry, Titanium), and may be regarded as one of the usual constituents, having been very generally found associated with iron ores (A. A. Blair, Chemical Analysis of Iron, 1888, p. 193).

All of the rocks and minerals from Berks, Montgomery and Philadelphia counties (Pa.), syenite, dolerite, gneiss, pyroxene, schist, hornblende, the rock formation of the famous Cornwall mines (Pa.), contain titanic acid in quantities from 0.50% to 5% and more (Geological Survey of Pennsylvania Cb., p. 61). It exists in the clays and slate clays of York, Adams and Lancaster counties (Pa.), in which it is to be regarded as an essential component, its amount being remarkably constant (Am. Inst. of Min. Eng., 6, p. 190).

From rocks it finds its way into ores. In *New Jersey* the very general presence of this element in the clays and some of the gneiss rocks has led to the belief that it is rarely absent from iron ores and nearly all of the later analyses of ores of this State since 1870 show its presence from traces to 11.60% and more of  $\text{TiO}_2$  (Geological Survey of New Jersey, 1879, p. 152), and still some of these ores, considered amongst the finest of the country, have been and are daily smelted in blast furnaces in Pennsylvania and New Jersey in admixture with other ores. The Dickerson mine, one of the very best, contains 0.79%  $\text{TiO}_2$ , the Mount

Pleasant 0.58%, the Teebo 0.59%, the Hibernia mine 0.55% (Am. Inst. Min. Eng., Vol. XIV.). The Ringwood mines (Passaic Co.), worked since the last century, and belonging now to Messrs. Cooper & Hewitt, have supplied for years the ores used in the Durham and Ringwood furnaces (Am. Inst. Min. Eng., Vol. XIV.). They contain from 0.30% to 2.72%  $\text{TiO}_2$  (Geological Survey of New Jersey, 1873, p. 53). Other ores containing 11.60%  $\text{TiO}_2$  have been smelted in the same furnaces or in others in admixture (Ib., 1873, p. 55, *et seq.*). Ores from New Jersey containing 6.23%, 8.21%, 11.60%  $\text{TiO}_2$  have been smelted alone in a blast furnace for several months, or nearly one year (personal information from the manager of the furnace).

Iron ores of many districts of *Norway* and *Sweden*, forming enormous, almost unlimited deposits, and containing in some cases 25 to 45% of  $\text{TiO}_2$  are waiting for the development of an industry which only the lack of combustibles other than charcoal impedes (Journal of British Iron and Steel Institute, 1880, p. 132); many of them have been smelted in these countries and some have been imported to England for treatment. It is present in the ores of the district of Ivenköping (Sweden), to the extent of 6.37%  $\text{TiO}_2$ , yet these ores are smelted alone in the blast furnaces of this region furnishing one of the well known brands of Swedish iron (Jordan, *Revue de l'Exposition Universelle*, 1867, p. 155, II.); in the ores of Newbottom district 9.10%  $\text{TiO}_2$ , of the Norland province, Ulfo, 9.50%  $\text{TiO}_2$ , of Kronaberg district 8.50%  $\text{TiO}_2$  (Report of the U. S. Commissioner to the Vienna Exhibition, 1873, p. 182), and in many other ores of that country and Norway 7.10% to 15.10% and 40.80%  $\text{TiO}_2$  (Prof. Forbes, *Jour. of Br. Ir. and St. Inst.*, 1880).

It is found in *Russian ores* smelted in blast furnaces in the Ural district (4.06% to 4.86%  $\text{TiO}_2$ ); this district manufactures 18,000 tons of pig metal per year (*Revue de l'Exposition Universelle de 1867*, p. 548, III., Jordan); in ores smelted in *Bavaria* in the blast furnaces of Hochstein and Eisenberg (Munzerheim ores) 1.396%  $\text{TiO}_2$  (Ib., p. 594, III.). A slag of the Concordia Iron Works (Coblentz), contained 6.70%  $\text{TiO}_2$  (Percy's *Metallurgy*, p. 515); that of a Styrian charcoal furnace 6.71%  $\text{TiO}_2$ .

(Osborn's Metallurgy, p. 128); that of a Swedish furnace, Ezerholm, 9.20%  $\text{TiO}_2$  (Ib.) (Vathaire les Hauts Fourneaux). It is found in Antrim and other *Irish bog ores*, aluminous ores, in quantities varying from 3.51% to 5%  $\text{TiO}_2$  (Percy's Metallurgy, p. 207, 225), ores extensively imported into the United States by furnaces in Pennsylvania, and elsewhere here and in England smelted in admixture with other ores (Kimball, Am. Inst. Min. Eng., Vol. IX., p. 14). The Irish Hill Mining Co. ores contain 5.80 to 6.20%  $\text{TiO}_2$  (Chemical News, 1881, p. 294), (Encyclopedia Britannica, p. 81).

It is found in bauxites (*France* and elsewhere), mixed as a flux with other ores, 3.20%  $\text{TiO}_2$  (Ib.). In *Algeria*, Oran province ores 1.25%  $\text{TiO}_2$ , in *Sardinia*, Iglesias ores 1.25%  $\text{TiO}_2$  (Vathaire les Hauts Fourneaux). In many iron sands of *Sicily* 8.90%  $\text{TiO}_2$  (Revue de l'Exposition Universelle, 1867), (Bauerman's Metallurgy), and in *New Zealand* (Ibidem).

It is found in *Pennsylvania ores* in quantities of 0.30%  $\text{TiO}_2$ , in McIlvee ores, York Co. (Geological Survey of Penn. MM., p. 227), in Chestnut Hill ore bank, mined by the Berks Co. Mining Company, 3.93%  $\text{TiO}_2$  (Ib., MM., p. 229), in Brandywine ores 10.44%  $\text{TiO}_2$ , smelted in blast furnace without any trouble in admixture with others in the proportion of 12% in the charge, about 1.25%  $\text{TiO}_2$ , average; in the magnetic sands of Adams Co. 7.37%  $\text{TiO}_2$  (Geolog. Sur. of Penn., M. 3, p. 101, MM., p. 227 *et seq.*).

It is found in *New York State* ores almost constantly (10th Census of the United States, Vol. XV., p. 555, 556, etc.), in Chateaugay ores 0.47%  $\text{TiO}_2$  smelted in blast furnaces (Am. Inst. of Min. Eng., p. 81, Vol. IX.), in ores of the northern part of the State 0.733%  $\text{TiO}_2$  (Ib., Vol. XIV.), in Lake Champlain ores, Westport,  $\text{TiO}_2$  4.58% (Ib., Vol. XI., p. 159), split rock 14.70%  $\text{TiO}_2$  (Ib., Vol. II., 1873, p. 13), used in blast furnaces in admixture. In ores from Oneida Co., Kirkland ores, 10 to 40%  $\text{TiO}_2$ , smelted in admixture in the Coleraine furnaces. In Westchester Co. aluminous ores 2.41% to 4.41%  $\text{TiO}_2$ , recommended in admixture with others (Kimball Ib., Vol. IX., p. 14), in limonites of Staten Island (10th Census of the U. S., p. 124).

In *North Carolina ores* in proportions varying from 12.08% to 13.71%  $\text{TiO}_2$  (10th Census U. S., p. 311), and up to 38.61% (Ib.,

p. 562), in Cranberry ore banks 0.95 titanic acid, in Chatham Co. ores 1.04%  $\text{TiO}_2$ , in Mitchell Co. ores 0.95%  $\text{TiO}_2$ , up to 5.33%, metallic iron 65.44%, Roan Mountain ores (Am. Inst. Min. Eng., Vol. XI., p. 159), in Centre Co. ores 8.65%  $\text{TiO}_2$ , metallic iron 60.88% (10th Census), (Am. Inst. Min. Eng., Vol. XI.).

In Colorado ores, in quantities of 11.99%, 11.61%, 12.92%, 12.73%, 13.84%, 14.86%, 13.06%  $\text{TiO}_2$ , in different districts (10th Census U. S., p. 476).

In *Oregon* ores. Putnam Co., Oswego Furnace smelts ores containing 0.54%  $\text{TiO}_2$ . In ores of Clackamas Co. and of other districts in which its presence was ascertained but quantities not determined (10th Census, p. 566).

In *Rhode Island* ores, Iron Hill Mine, Providence Co., 9.35%  $\text{TiO}_2$ .

In *Virginia* ores, in which it is "present" in almost all the ores in quantities not determined, in some  $\text{TiO}_2$ , 0.16% (10th Census, p. 267-576) and up to 6.53%  $\text{TiO}_2$ , metallic iron 52.20% in North Garden ores (Am. Inst. of Min. Eng., 6, p. 159).

In *South Carolina* ores, Silver Mountain bank, York Co.,  $\text{TiO}_2$  39.67% (10th Census U. S., p. 267-576, etc.). In many other ores of different States its "presence" is "quoted" but without any amount being given (10th Census U. S.). In some analyses it may figure in the "*Insoluble Residue and Silicious matters*," but no analysis of the latter is given (Geological Survey of Pennsylvania and of other States).

It has been found in the *Canadian* ores, 11.27%  $\text{TiO}_2$ . (Revue de l'Exposition Universelle de 1867, p. 685), in the Bay St. Paul ores, 48.60%  $\text{TiO}_2$  smelted in two blast furnaces in 1873 furnishing an excellent iron (Mr. Riley, Jour. Br. Ir. & St. Inst., 1874, p. 132), they constitute the mineral ilmenite (Am. Inst. Min. Eng., II., p. 13), in Moisie River sands, 4.15% to 28.95%  $\text{TiO}_2$  (Bauerman's Metallurgy, p. 53, *et seq.*) (Chemical News).

It is a constant element in the *English* ores smelted in the Cleveland district in the furnaces of Sir Lothian Bell and others. The Cleveland ores contain a good deal of titanium (Mr. Riley, Jour. Br. Ir. & St. Inst., 1874, p. 132), while in the Northhamshire it is found most readily, even in the cinders. In fact, titanic acid



occurs in all clays. It is a *very common material*, very difficult to find; it has a great tendency to *stick to the iron, and has been very often estimated as oxide of iron and mistaken for it* (Mr. Riley, *Ib.*, p. 132, *et seq.*).

It has been found frequently in the U. S., in the Lehigh furnaces, in the crevices of the hearth after the furnace had been blown out. As for instance at the Crane Iron Works, and pig iron from the same works was *colored purple by the presence of titanium*; the ores containing titanium were from Morris Co., New Jersey (Osborn's Metallurgy, p. 485).

It would appear from the preceding quotations that titanium is not a rare element, nor one confined to special localities or countries; in fact, it is met with in a number of iron ores here and in Europe and Africa, etc., in quantities from traces to 50% of  $\text{TiO}_2$ . That some of these ores, at least, have been smelted in blast furnaces sufficiently appears from the above, and from the fact that many pig irons both here and in Europe contain it as a constant element in very notable quantities, and have contained it for years without any mention being made of troubles resulting from the use of such ores in a blast furnace or from the slags run with these pigs, which slags did also contain titanium, as we will see further.

When a proportion of titaniferous ore is added to the charge, it increases the strength of the metal, at the same time giving it a peculiar mottled character (Bauerman's Metallurgy, 1874, p. 53). Titanium may be present in pig iron to the extent of about 1% (1.64%  $\text{TiO}_2$ ); its presence was considered as a very favorable factor (*Ib.*).

Pig irons containing 0.47%, 0.71%, 1.15% titanium, corresponding to 0.77%, 1.16%, 1.88%  $\text{TiO}_2$ , have been regularly produced in English furnaces from a mixture of  $7\frac{1}{2}\%$  ilmenite, containing 38.84%  $\text{TiO}_2$  with red hematites and local ores, which supposes in the mixture an average of about 2.913%  $\text{TiO}_2$ , admitting that the *local* ores did not contain any (Percy's Metallurgy, p. 551). Sir Lothian Bell has obtained from regular mixture of *English local ores* used daily in the furnaces of the Cleveland district,  $\frac{1}{3}$  Cornish ore,  $\frac{1}{3}$  red hematite,  $\frac{1}{3}$  Irish bog ore, pig irons containing respectively,

0.79%, 1.15%, 1.629% titanium, corresponding to 1.29%, 1.88%, 2.87%  $\text{TiO}_2$  (Percy's Metallurgy, p. 552), (Memoir of Lothian Bell to the British Association, 1863), and the slag run with these pigs contained 0.75%  $\text{TiO}_2$  (Percy's Metallurgy, French translation under the auspices of the author, 1865), (Memoir of Lothian Bell, 1863), (Phenomena of Iron Smelting, L. Bell, 1873).

Cleveland pigs contain titanium in a regular and constant manner as a *normal constituent*, as analyses show, in quantities of 0.09%, 0.13%, 0.14%, 0.20%, 0.22%, 0.26%, 0.51%, 0.56%, corresponding to 0.15%, 0.21%, 0.23%, 0.33%, 0.36%, 0.42%, 0.84%, 0.92%  $\text{TiO}_2$ , and up to 1% titanium (1.64  $\text{TiO}_2$ ), and *above* (Percy's Metallurgy, French Translation), (Memoir Lothian Bell, 1863), (J. of B. Ir. & St. Inst.). Mr. Riley says (J. of Br. Ir. & St. Inst., 1880, p. 190), titanium is *always present* in fair amounts up to 1% (1.64  $\text{TiO}_2$ ), but rarely above that in Bessemer or *Cleveland* pig; it is *always* found in Bessemer pig. In the discussion of the paper which has given rise to these observations, not the slightest mention is made of troubles resulting for the furnace from the normal and daily use of ores capable of supplying the above percentages of  $\text{TiO}_2$  to the pig, and the English furnaces, as is well known, have longer runs than the American, a run of eight years or more not being a rare case with the former.

Pig irons *smelted in this country* have shown titanium also as a pretty constant element, and the examples quoted below could be multiplied. The analyses were made by Messrs. Drown and Shirmer (Am. Inst. Min. Eng., 17, p. 346).

<i>Pig Irons.</i>	<i>Titanium.</i>	<i>Titanic Acid.</i>
Richmond,	0.018	0.030
Greenwood,	0.052	0.084
Hecla,	0.048	0.080
Dutchess,	0.055	0.090
Glendon,	0.099	0.160
Silver Gray,	0.114	0.190
Leesport,	0.115	0.191
Bushong,	0.225	0.370
Unknown,	0.318	0.520
* Perryville,	0.040	0.066

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\*This latter pig was analyzed by the writer.

Ores containing less than 3½% of titanic acid are not recognized any more as titaniferous ores (Dana's Mineralogy). Ore containing 39.20%  $\text{TiO}_2$ , ilmenite, have been successfully worked for several years at Norton (England) by the Norwegian Titanic Iron Co. The slag run from the furnace contained 36.18%  $\text{TiO}_2$ , and 27.83% silica. The uncertainty of importation, the leanness of the ores, which contained only 32 to 36.31% iron, the amount of coal necessary to run in slag such an enormous amount of silica and titanic acid (64.01%) prevented the scheme from being financially profitable after a few years. But the metallurgy of the treatment was a success, and showed that, with proper management, a furnace can carry such a percentage of titanic acid in the charges without clogging (Wm. H. Bowren, Am. Inst. Min. Eng., 11, p. 159), (Osborn Metallurgy, p. 474). The Canadian Titanic Ore Co. smelted in two blast furnaces ores from Bay St. Paul quoted above, containing 49.60%  $\text{TiO}_2$ , without any trouble in the furnaces. The ores were very lean (Mr. Riley, Journal of Br. Ir. & St. Inst., 1874, p. 132; 1876, p. 190).

A good liquid slag can be obtained *without any difficulty* with ores containing 3.55%  $\text{TiO}_2$  (Prof. Forbes Am. Inst. of Min. Eng., Vol. XI., p. 159). With proper charges and fluxes, with an amount of titanic acid not above 8%, it is not difficult to work an ore *cleanly* and *profitably* (Ib.). With an acid cinder and a slack blast, ores containing from 8 to 13%  $\text{TiO}_2$  can be readily treated without any trouble (Ibidem). (Chemical News, Dec. 11, 1888.) These are the statements and practice of an eminent chemist and metallurgist who has been for years consulting engineer for blast furnace managers in Sweden, Norway and England, who has supervised the running of many furnaces in Sweden and Norway, smelting titaniferous ores, and the furnace at Norton (England), treating the ilmenite from Norway mentioned above.

Although troublesome when present in large quantities and having a tendency to render the slags pasty, in working the furnace to a certain kind of pig and not at a too high temperature, the *fluxes* of the furnace require but *very little foreign matters* in working with titaniferous ores (Osborn Metallurgy, p. 431).

Scandinavian iron masters have often expressed to Prof. Forbes

their surprise at the want of information possessed by English metallurgists in general upon the subject of highly titaniferous ores, containing such percentages as 25% to 40% titanic acid. Their experience has shown that the only objection to the use of such ores is that they are found to be more or less refractory, as they contain a greater percentage of titanic acid, and if much titanium is present they require a quantity of coal so much larger to smelt them as to render their employment alone not profitable when ores free from titanium can be obtained cheaply in the district. After considerable experience in smelting these ores, the Norwegian ilmenite and others which yield a very good iron, it was not found profitable to smelt them alone for the preceding reasons, but their use was found beneficial when employed in about equal proportions with the other ores of the district free from titanium (Prof. Forbes, J. Br. Ir. & St. Inst., 1877, Vol. XI.).

Titanium iron is essentially a forge iron. A furnace that can make iron under an acid cinder and a slack blast and keep the silica out will *not be troubled with titanium deposits*; the details of furnaces for smelting these ores are like those suitable for ordinary hematites or magnetites (Am. Inst. Min. Eng., 1877, 2.) Titanic acid is also found in slags. Slags containing 0.75%  $\text{TiO}_2$  have been run in the Cleveland district from the smelting of local ores (Percy's French Translation) (*Revue de l'Exposition Universelle*, p. 37). The Concordia iron works slag, quoted by Percy (see above), contained 6.70%  $\text{TiO}_2$ ; one quoted by Osborn as run from a styrian charcoal furnace the same; a slag from Ekersholm, Smoland district (Sweden), contained 9.00%  $\text{TiO}_2$  (Osborn), (Vathaire, Les Hauts Fourneaux, p. 41). Blast furnace slags contain titanic acid when treating titanic ores. It is combined with the bases and silica. It does not notably change the appearance of the slag and nothing but an analysis can discover its presence. It gives a violet coloration to the cinder, the shade of which is more blue than that due to oxide of manganese, but this blue coloration can be imparted to the silicates by so many different causes, that it cannot be considered as a proof of the presence of titanic acid (Rivot's Docimacy, p. 157), (*Revue de l'Exposition Universelle*, 1867, Swedish ores).

When smelting titaniferous ores with white iron *most of the titanic acid enters the slag*, the pig iron is said to yield an excellent wrought iron and steel, and as little titanium is found in these products, it must be due to the indirect beneficial effect of smelting ores containing titanic acid (Wm. Crooke's Adaptation from the German Edition of Prof. Kerhl's Metallurgy, London, 1869, p. 316). About 1% titanium ( $1.64 \text{ TiO}_2$ ) may be present in the pig, it increases the strength of the metal (Ib., p. 317).

The iron obtained at Norton (England) from Norwegian ilmenite was found to be extremely strong and was used in Europe for armor plates commanding three times the price of ordinary iron (Osborn's Metallurgy, p. 474).

This Norton iron obtained from ilmenite containing 40.95% titanic acid, 39.20% as average of cargo, went to the armor plates of Sheffield on account of the toughness which this iron not only possessed but imparts to other iron in admixture in the puddling furnaces. When rolled into plates and merchant bars it possesses such a *clean, soft, tough nature* as should render it invaluable for boiler plates, sheets of cold stamping and kindred uses . . . and ores now useless could be made of vast service to the iron trade and to the industries (Mr. Deby, Secretary Br. Ir. & St. Association, 2, p. 19, 1877).

Titanium is found in very variable proportions in certain pig iron, to which it appears to communicate a great tenacity (Rivot's Docimacie, p. 156). It increases the strength of the metal (Bauerman, p. 53). Ores containing titanium may be considered very favorable for the manufacture of pig metal; in many respects they are preferable to the spathic ores, for, with very little attention they will produce white iron rich in carbon, the very material required for German steel (Osborn Metallurgy, p. 431).

In Sweden it is a common practice to add 10% of titaniferous ores to the charges to remove sulphur. Whatever may be the reason of this effect, what is known with certainty is that titanic ores in the U. S., Canada, New Zealand, Sweden and Norway, are such that the metal produced from them is wonderfully good (Dr. Forbes, J. of Br. Ir. & St. Inst., 1874, p. 131). Titaniferous

ores containing 48%  $\text{TiO}_2$  smelted in Canada have furnished an *excellent pig* (Mr. Riley, *Ib.*, p. 132).

In Norway and Sweden the ores of Krager and Eger, containing 15% and 7.10%  $\text{TiO}_2$  respectively, are worked in blast furnaces. If ores do not contain more than 8%  $\text{TiO}_2$  their reduction is not difficult and the product is of good quality. An examination of the ores analyzed in this report (Report 1879 Geological Survey of New Jersey) shows the presence of titanitic acid in these New Jersey ores from traces to 5%  $\text{TiO}_2$ . These are *all* used successfully and are said to *make good iron* (Prof. Cook, *Geology of New Jersey*, 1879, p. 152).

The New Jersey ores, containing 11.60%, 6.23%, 8.21%  $\text{TiO}_2$ , and averaging about 8.50%  $\text{TiO}_2$  in the charges, have been smelted alone in a blast furnace for nearly one year and have yielded a pig iron of a "*remarkable strength*," "which could almost be bent in two without breaking." The cast iron was graphitic and considered an exceptionally good No. 1 gray foundry iron. It commanded, it is claimed, one dollar more per ton (personal information).

Putting aside the questions of the *improvement and good qualities claimed* for the iron obtained from titaniferous ores, the practice in Europe and even in this country, within certain limits, seems to establish the fact that titanium cannot be considered as being *always* and *necessarily* a cause of trouble in the blast furnace if properly dealt with, even when present in very large quantities, since ores containing as much as 40%, and even 48%, of titanitic acid have been smelted, in known cases, for several years in the same furnace as *successfully*, if not as profitably, as others richer in iron and free from titanium or containing lesser proportions of it. On the other hand, certain blast furnace managers in this country go as far as to maintain that *inappreciable quantities*, mere traces of titanitic acid, are sufficient to interfere with the good working of a furnace—clogging and stopping it. Others, a little more liberal, will not even admit a limit of 0.25% of titanitic acid in an iron ore, nor will they consider it practicable to use it in a blast furnace. For them the smaller percentage is as deleterious as the

larger, the only difference being that the action is smaller and that it requires a longer time to fill up the furnace. To these extremists it might be answered that, unconsciously, then, many iron masters have produced in this country, daily and normally, pig irons in which the quantity of titanium has reached as much as 0.318%, corresponding to 0.52%  $\text{TiO}_2$  (from 0.03% to 0.52%, considering *only* the analysis given above). All of these proportions, according to their view, the smallest as well as the largest, were sufficient to have ultimately clogged the furnaces, and still the latter have had years of excellent running as regards economy and quality of product, at least some of them did have, since one of these pig irons, the "Bushong," containing 0.37%  $\text{TiO}_2$ , has commanded one dollar more per ton on the market.

Admitting that the ores smelted contained 50% of iron, that is, that two tons of ore were fluxed per ton of pig metal, a quantity of 0.52%  $\text{TiO}_2$  in the pig would correspond to 0.26% in the ores, and this supposes that there was none left to pass into the slag; how then could the latter be rendered *pasty* or *infusible*? Furthermore, if *all* the titanic acid is thus accounted for in the pig, none has been left in the furnace to clog it and we are in this dilemma: either some titanic acid *did* pass into the slag and the ores contained more than 0.26%  $\text{TiO}_2$  or *all of the titanic acid can be made to pass into the pig and thus leave the furnace*. That none was left in these furnaces, not even *traces*, if we adopt the views of these extremists, appears to be sufficiently proved by the fact that the pig irons analyzed were not special specimens, but the regular product of the iron works from which they came.

We find in England, in the Cleveland district, in Staffordshire and Northamptonshire, smelted daily from the regular local ores, normal pigs which, as Mr. Riley says, contain titanium in good quantity, up to one per cent. or more and occasionally as much as 1.6%, corresponding to 1.64% or even as much as 2.87%  $\text{TiO}_2$ , and the same authority adds, "Titanic acid is also found *most readily* even in the slags" of these districts. We have every reason then to suppose that the slags run with the American pigs quoted did *also* contain titanic acid. With materials 50% rich in iron the

preceding figures would correspond to at least 0.82% to 1.43%  $\text{TiO}_2$  in the English ores; with materials only 40% rich to, at least, 0.67% to 1.18% in the charges, and these English furnaces have much longer runs than the American. We know from analysis given by Percy and others that at least the "Irish bog ores" used about in proportion of one-third with the other local ores, contain (Antrim) 3.51% to 5%  $\text{TiO}_2$ . This would bring the proportion of titanic acid in the mixture to from 1.17 to 1.66%, or 0.70% to 1.00% titanium, figures which correspond very nearly with those found for titanium in the normal pigs of the district.

Even in this country certain iron masters more enterprising and more experienced than others have successfully disposed of several thousands of tons of ores containing from 9% to 15% titanic acid, average 12%, by smelting them in a mixture with other ores in such proportion that the average proportion of titanic acid was 0.38%, and with as much as 0.75% titanic acid in the mixture with proper care they did not experience any trouble.

They have gone so far as to state that, after many experiments with titanium, the result of their experience has been that a mixture containing a *greater percentage* of titanic acid *than 1.25%* could not be successfully used. This admits clearly a possible maximum limit, and is in complete contradiction with the assertions of the extremists. The following is another illustration of American practice. It covers a lapse of ten years' running of two blast furnaces. These furnaces used five different kinds of magnetites, all containing titanic acid in quantities varying from 0.33 to as much as 1.34%, as analyses made at the time and subsequent ones have proved. The ores averaged in admixture about 0.70% titanic acid. They were exclusively smelted for that period without any trouble whatever from deposits, sluggish slags or clogging. The furnaces had runs of three and three and a half years—a very good run in the United States—and they produced all grades of iron from white to gray No. 1, and even to graphitic iron. Titanic acid was detected in the slags. These two examples corroborate the results of the English practice. They are given here because we are particularly acquainted with the circumstances of each case and can substantiate these assertions.



If we pass to Sweden and Norway we find there ores containing 5% to 10%  $\text{TiO}_2$ , smelted alone clearly and profitably in charcoal furnaces, others containing 15% to 20%  $\text{TiO}_2$  or more, smelted in admixture or even alone with a beneficial effect; and, lastly, Norway ores containing as much as 40%  $\text{TiO}_2$  and only only 36% of iron smelted by a company in England for a few years with a perfect success as far, at least, as the *metallurgy* of the treatment was concerned. No clogging or stoppage of the furnace, no pasty slags interfering with its working are mentioned. In Canada we notice results exactly similar with ores of nearly the same composition as the preceding Norway ore. We find slags in England and slags run from normal local ores containing 0.75%  $\text{TiO}_2$ , others quoted above containing 6.70% and 9%  $\text{TiO}_2$ , slags run from local ores containing enough titanic acid to supply to them these percentages. We find pig irons in England and in this country containing this element as a constant factor in quantities from 0.08 to 1.64% titanium and more. There seems to be a contradiction somewhere. Without pretending to settle the question by our own authority, we believe that enough facts have been presented to justify, at least, the following remarks:

Titanic acid, though present it may be said in almost all magnetites and hematites of certain districts, in various quantities, generally small, has been mostly *ignored* until a comparatively recent date. In the analyses given in the geological survey of New Jersey it does not figure until 1870, from which date it was *looked* for and found regularly in different quantities, from 0.30% to 1%, in ores in which its presence had not been previously suspected, and so constantly, from traces to 15%, in different ores from widely separated regions, that this fact has called for the statement of the late Prof. Cook, that it seems to be almost a normal element of the New Jersey ores (Geol. Sur. of N. J., 1879). As Mr. Riley has observed, its determination is very difficult, and it has been very often mistaken for *oxide of iron*. In the reports of the geological surveys of Pennsylvania, up to 1886-87 at least, most of the analyses are tabulated "Silica and insoluble residue," no composition of this residue is given. Titanic acid might and could have

been present there and entirely overlooked. (See Analyses of Geological Survey of Pennsylvania.)

Such a supposition is not a gratuitous one. In the analyses of iron ore given in the 10th Census of the U. S., we find, amongst other examples, p. 311, under the denomination of North Carolina ores, "Silica and insoluble residue, 28%," and in the subsequent analysis of these 28% of "residue," titanic acid appears for 11.82%, nearly half ! Such a proportion would have been completely ignored except for special analysis. In many other ores titanic acid figures only as "present."

Consequently, iron masters in Pennsylvania, New Jersey, and elsewhere must have been smelting for years, and are even smelting to the present day, in admixture with other ores or alone, local ores or magnetites and hematites from New Jersey, for which they have been satisfied to pay the best prices on account of their richness in iron, and in which titanic acid had not been suspected or its proportion determined up to 1870, and for others much later still. Yet, there has not been any complaint made of these ores on this score ; on the contrary, they have commanded a better market ; trouble has been taken to have them shipped to distant furnaces. We could quote many such ores, but limit ourselves to the Dickerson mine, 0.79%  $\text{TiO}_2$  ; Mt. Pleasant Mine, 0.58%  $\text{TiO}_2$  ; Teebo Mine, 0.59%  $\text{TiO}_2$ , all in Morris Co. ; the Ringwood Mines (Passaic Co.), 0.30 to 2.72%  $\text{TiO}_2$  ; the Hibernia Mine, 0.55%  $\text{TiO}_2$ . (See Geolog. Survey of N. J.) (Am. Inst. M. Eng.) In the analyses of the Dickerson Mine, Mt. Pleasant, Teebo, Hibernia, given in 1868 in the Geological Survey of New Jersey, titanic acid *does not appear, not having been sought for.*

The following analyses will give an idea of the value of these ores, those of Mt. Pleasant and Hibernia have been made by us, those of Ringwood Mines are taken from the Geol. Survey of N. J.:

FOUND.	MT. PLEASANT.		RINGWOOD.		HIBERNIA.	
	Rich ore.	Av. cargo.	I.	II.	I.	Av. Ore
Silica .....	1.60	8.17	3.00	5.80	5.90	8.87
Sulphur .....	0.07	0.09	3.00	5.80	0.05	8.87
Phosphoric acid .....	0.50	0.81	0.45	traces	1.05	1.15
Alumina .....	1.40	0.68	2.59	1.91	1.23	3.13
Oxide of iron .....	95.65	85.84	94.06	90.47	87.99	80.59
Oxide of manganese .....	0.07	0.06	0.25	90.47	0.06	80.59
Lime .....	0.50	2.21	1.57	90.47	2.57	3.44
Magnesia .....	0.40	1.53	0.22	0.72	1.23	1.50
Titanic acid .....	0.58	0.58	0.30	2.72	0.55	0.55
Metallic iron .....	69.27%	62.10%	65.84%	63.29%	63.72%	58.36%
Observations .....	Iron is in the ore as Magnetic oxide.		Iron as Ferric oxide.		Magnetic oxide.	Analysis by L.L. Biere-with.

Is titanic acid, then, *always* and *in all quantities* an objectionable element in an iron ore? Is it not more correct to say that, within certain limits, which we may perhaps fix at 1.00% or more, it has proved little objectionable; on the contrary, that it has passed for years unnoticed? No disturbances have occurred in the running of the furnaces unknowingly smelting such titaniferous ores to call attention to a detrimental element. So much seems to be assured, and confirmed by the English practice. Above these quantities what is the limit at which its presence in an iron ore would begin to be felt by its effect upon the running of the furnace in respect to economy or at which the judicious treatment, such as a change in the routine of the charges and fluxes adopted for non-titaniferous ores, might become

necessary to insure both economy and success? American furnaces may have unconsciously worked ores containing much more titanitic acid than 1 or 1.25%, and some have done so to our positive knowledge (8% to 10% titanitic acid in the charges, as derived, at least, from verbal assurances of certain iron masters), without experiencing any particular troubles, but in the absence of direct and well authenticated practice, and especially of *regular analyses of the charges* in the case alluded to, it may not be fair to draw a conclusion.

If, as stated by Dana, an ore ceases to be recognized as titaniferous when it contains less than  $3\frac{1}{2}\%$   $\text{TiO}_2$ , this figure might be called the limit, and the personal observations of Prof. Forbes affords a corroboration of this statement. Beyond that, if we take to guide us the European practice in Norway and Sweden, the examples quoted above would prove that, with proper fluxes, even regular titanitic acid minerals, such as ilmenite, containing from 40 to 48% of this substance, can be and have been cleanly and successfully smelted in furnaces without any disorders resulting in the latter from their use. The question of economy in the particular case mentioned depended on many factors and, at any rate, has nothing to do with the metallurgy of the treatment.

If dealt with as corresponding proportions of silica would be when present in ores in very notable quantities, titanium has certainly a tendency to produce "deposits" and to render the slags less fusible. All depends on the judicious and rational choice and proportion of the fluxes to obtain a desired result. "Nothing economical or skillful can be accomplished when the charges are badly engineered (Osborn's Metallurgy, p. 478); the skill of a blast furnace manager as a metallurgist consists mainly in forming a fluid slag with the materials at his command (J. of Br. Ir. and St. Inst., 1874, p. 75). Certain natural compounds of titanium, such as sphene, calcium silico-titanate and kailhaite, are perfectly fusible in a blast furnace. (Ib., p. 43.) Their composition is as follows:

	SPHENE.				KEILHAU- ITE.
	I.	II.	III.	Average.	
Silica .....	32.26	31.90	31.20	31.78	31.33
Titanic acid..	38.57	40.60	40.92	40.00	28.04
Lime.....	27.65	25.89	22.25	24.59	19.56
Oxide of iron.	0.76	1.61	5.06	2.00	6.57
Alumina.....	0.76	1.61	5.06	2.00	8.03
	(Pied- mont) Rivot.	Dana. Rivot.	(Arendal) Rivot.	Average of these 3 analyses.	Dana.

So eminent a chemist and metallurgist as Prof. Forbes has certainly cleared this question from all possible doubts by his practice. He has smelted, without admixture, ores containing 40% titanic acid without any trouble in the furnace. We refer to the excellent papers of Mr. W. M. Bowren (Am. Inst. Min. Eng., 9, 159), and to that of Mr. Deby (J. of Br. Ir. and St. Inst., 2, 1877, p. 13) for the details of the operation. The ores treated were the Norway ilmenite, of which an average analysis of a cargo gave (see papers quoted) :

Titanic acid .....	39.20	} The composition of the slag actually run from the fur- nace, as given in the paper alluded to, approximated, as closely as can be obtained in practice, the composition of <i>sphene</i> , a <i>natural mineral of</i> <i>titanium</i> , fusible in the blast furnace. This is what good management can do.
Ferric oxide .....	18.59	
Ferrous oxide.....	30.00	
Alumina.....	2.89	
Manganous oxide.....	0.60	
Silica .....	5.70	
Loss .....	0.22	

Iron=36.3%.

Composition of Slag.		Average Sphene.
Silica - - - -	27.83	31.78
Titanic acid - -	36.18	40.00
Lime - - - -	24.36	24.59
Oxide of iron - -	1.86	2.00
Alumina - - -	9.18	"
Magnesia - - -	0.60	"

As it can be calculated from the preceding analyses and from the charges of the furnace as given in Mr. Bowren's paper, *all the titanic acid* of the ore is accounted for and has mostly been made to pass into the slag, excepting the small percentage left in the pig metal, perhaps 1 to 2%, and, of course, titanium having left the furnace it could not in any manner be the cause of obstruction by hangings or deposits.

If these results were not as economically obtained as with other ores free from titanium, it may be a question if the higher prices realized for the products were not a compensation for the extra expense of combustible, or would not be if the ore, though containing as much titanic acid, had been richer in iron; but it is useless to discuss this side of the question; the *possibility* of smelting successfully and cleanly such highly titaniferous ores is all that we intended to establish beyond dispute. The objections to the presence of titanic acid in an iron ore would thus be entirely modified if we adopt the conclusions of Prof. Forbes and the results of his practice and of that of the Swedish metallurgists. *It would be no longer a question of "clogging of the furnace" but simply one of economy in each case.*

Reduced to this it would seem that such small quantities as 1 to 1.25%, or even more, of titanic acid could not be objectionable on this score, especially if these titaniferous ores present, as they do, such characters as render them very valuable otherwise.

Prof. Forbes (J. of Br. Ir. and St. Inst., 1877, p. 132) has called attention to the fact that ores of this kind, in Norway, Sweden, Canada and New Zealand, are remarkably *free from phosphorus* and very frequently also from sulphur; though not absolutely and invariably so, still, as a rule, real titanic ores are extremely free from these elements, and when they are not, the question may

be raised, does not the phosphoric acid come from adhering barren gangue of apatite and not from the *ore itself*? Mr. Riley (Ib.) commenting on these remarks of Dr. Forbes has fully confirmed his assertions. It is quite exceptional (says he) to find titaniferous ores containing any phosphorus. The same observations have been made independently, in 1875, by Prof. Cook for the titaniferous ores of New Jersey (Geol. Survey of N. J., 1875, p. 35). Analyses (he says) indicate this curious relation between titanium and phosphorus, that a considerable percentage of the former always corresponds to a very *small* amount of the latter. The behavior of such ores in the blast furnace and the character of the product might be an interesting point in the metallurgy of iron, and the chemical examination of iron ores to test this hypothesis further or substantiate these facts ought to be continued.

It was true with the ores smelted in the two furnaces we have spoken of as having run for ten years, that those containing *least* phosphorus contained most titanic acid, as analyses showed:

	I.	II.	III.	IV.
Average Phosphorus - -	0.064	0.160	0.270	0.730
Do. Titanic acid - -	0.98	0.90	0.58	0.33

We have collected a number of analyses of ores coming from mines separated by the Atlantic or by distances on land still greater, which we give below. Any idea of fortuitous coincidence has to be excluded, and still the results seem to corroborate, in a remarkable manner, the above observations.

## UNITED STATES.

*Pennsylvania.*

1. McElvee ore - - -	TiO <sub>2</sub>	0.33%	P. 0.013	Met. Iron 68.50%
2. Chestnut Hill ore - -	"	3.93%	traces	" 63.75
3. Cornwall ore - - -	"	7.37	traces	— —

(Geolog. Survey of Pa., M3.)

*North Carolina.*

1. Rockingham Co.	TiO <sub>2</sub>	13.71%	P. .052	{ J. of Iron & St. Inst., 2, p. 13. 10th Census U. S., p. 311-326-561.
2. —	"	38.61	traces	
3. —	"	0.95	0.007	

*New York.*

1.	-	-	TiO <sub>2</sub>	2.41%	P. 0.095	} Weschester Co. Ores. Vol. 9, Am. Inst. M. Eng.
2.	-	-	"	3.88	" 0.07	
3.	-	-	"	3.52	" 0.04	
4.	-	-	"	3.90	" none	
5.	-	-	"	3.51	" traces	
6.	-	-	"	4.41	" 0.07	} 10th Census, p. 311, etc. Am. Inst. M. Eng., 14. Chateaugay, Ib.. 9. Iron, 60.46%.
7.	-	-	"	10 to 40%	" traces	
8.	-	-	"	0.733	" 0.021	
9.	-	-	"	0.470	" 0.02	

*Colorado.*

1.	-	-	TiO <sub>2</sub>	11.99%	P. 0.025	} 10th Census, p. 476.
2.	-	-	"	12.92	" 0.026	
3.	-	-	"	11.61	" 0.037	
4.	-	-	"	12.73	" 0.011	
5.	-	-	"	13.84	" 0.040	
6.	-	-	"	14.86	" 0.039	
7.	-	-	"	13.04	" 0.039	

*Oregon.*

1.	-	-	TiO <sub>2</sub>	0.54%	P. 0.006	} 10th Census, p. 566. Oswego Furnace.
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*South Carolina.*

1.	-	-	TiO <sub>2</sub>	39.67%	P. traces	10th Census. York Co.
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*New Jersey.*

1.	-	-	TiO <sub>2</sub>	7.70%	P. 0.04%	Iron 64.46	} Geological Survey of N. Jersey.— Ores from dif- ferent counties.
2.	-	-	"	1.00	" traces	do. 64.90	
3.	-	-	"	7.50	" 0.07	do. 65.52	
4.	-	-	"	9.80	" 0.04	do. 62.23	
5.	-	-	"	3.60	" traces	do. 67.10	
6.	-	-	"	11.60	" traces		
7.	-	-	"	4.70	" traces		
8.	-	-	"	5.90	" traces	do. 52.00	
9.	-	-	"	2.72	" traces	do. 63.33	
10.	-	-	"	1.95	" 0.06		
11.	-	-	"	1.95	" traces	do. 67.20	
12.	-	-	"	4.40	" 0.09	do. 53.00	
13.	-	-	"	1.00	" traces	do. 64.95	
14.	-	-	"	4.95	" 0.08		
15.	-	-	"	1.45	" traces		
16.	-	-	"	5.00	" 0.08		
17.	-	-	"	1.30	" 0.06		



**SWEDEN.**

- |    |   |                  |       |           |   |
|----|---|------------------|-------|-----------|---|
| 1. | - | TiO <sub>2</sub> | 6.37% | P. 0.023% | { Ivenkoeping. (Revue de l'Exp.<br>Univ., p. 155, II.)<br>J. of Br. Ir. & St. Institute, 1880,<br>p. 132.<br>And many others. |
| 2. | - | "                | 15.10 | " traces  |   |
| 3. | - | "                | 40.90 | " traces  |   |

## NORWAY.

1. Ilmenite,  $\text{TiO}_2$ , 39.20 (average); P., none, and many other ores containing it in various proportions are remarkably free from P. (Journal of Iron and Steel Institute, 1879-1880.)

**BAVARIA.**

1.  $\text{TiO}_2$ , 1.396% P. 0.12      Revue Exposition, p. 594, III.

**RUSSIA.**

1.  $\text{TiO}_2$  4.86% P. none Iron 63.00. Ib., p. 548.  
Ural District.

**SICILY.**

1. Iron sands,  $\text{TiO}_2$  8.90% P. none. Ib.

FRANCE.

1. Bauxite,  $\text{TiO}_2$  3.20% and above. P. none. Encycl. Brit.

## CANADA ORES.

- |   |                  |       |          |           |   |
|---|------------------|-------|----------|-----------|---|
| 1.  | TiO <sub>2</sub> | 48.50 | P. none  | {         | Bay St. Paul (Am. I. M. E.). (J. of Br. Ir. & S. Inst.)   |
| 2.  | "                | 4.83  | " traces |           | Moiste River (Bauerman). (Revue                           |
| 3.  | "                | 16.00 | " none   | {         | Exposition.)  |
| 4.  | "                | 2.34  | " traces |           | Iron 68.34%   |
| 5.  | "                | 3.17  | " 0.07   | do. 66.98 | { Ontario Ores, p.214-321.<br>(J.of Br. Ir. & St. In.'81) |
| 6.  | "                | 2.12  | " 0.052  | do. 63.88 | { Ilay Cook Mine, Ottawa.<br>(Am.-I. Min. Eng., 12.)      |
| 7.  | "                | 0.73  | " 0.07   | {         | Snowden, township near Toronto.<br>(Ib.)                  |
| (?) Ores carried to Cleveland, Ohio, and smelted there. |                  |       |          |           |   |

## IRISH ORES.

1. Antrim (Percy),  $\text{TiO}_2$  3.51 P. traces.

## NEW ZEALAND.

- |                  |   |   |   |   |   |                  |       |           |          |
|------------------|---|---|---|---|---|------------------|-------|-----------|----------|
| 1.               | - | - | - | - | - | TiO <sub>2</sub> | 6.17% | P. traces |          |
| 2.               | - | - | - | - | - | "                | 11.43 | do. none. | Iron 61% |
| (Chemical News.) |   |   |   |   |   |                  |       |           |          |

Unfortunately in many analyses of ores published in the 10th Census titanium is given as "present;" but as the amount has not been determined, it is impossible to conclude as to the coincidence between absence of P. and presence of titanium. In many others the "insoluble residue" is only given and all deductions are presented. At any rate, many ores remarkably free from phosphorus (and very often from sulphur also), as it appears from the above analyses, and also very rich in iron, now piled up on the banks of the mines or not mined to any extent, could be advantageously smelted and made available for Bessemer pigs, if, as the European practice tends to show, and as the American practice corroborates within certain limited amounts, perhaps, the objections to the use of titaniferous ores in a blast furnace were as much of a prejudice, in a general manner, as those which have been raised against the use of magnesia as a flux. "Titanium does not melt in any heat of a blast furnace" (Robert Hunt, Dict. of A. M. & Mines, 1878).

Possibly the prejudices of the extremists against the use of ores containing *any quantity* of this element did originally arise from a knowledge of this fact; but this does not prevent certain titanium compounds from being perfectly fusible, as we have had occasion to observe in respect to magnesia, lime or alumina. If furnaces working ores or materials containing titanic acid in limited quantities have experienced serious troubles the question may be asked: May it not be "*post hoc*," although not "*propter hoc*."

Resuming the above, we submit the following conclusions:

1°. Titanic acid is not *necessarily* and *always* a cause of trouble in the blast furnace, even if present in large quantities.

2°. In small quantities its presence appears to have been ignored for many years, and furnaces have run and do run to-day with ores rich in iron, containing as much as from 0.30% to about 1% titanic acid in the charges without apparent trouble of any kind, these ores being smelted alone or in admixture with others more or less free from titanium.

3°. When present in very notable quantities it has a tendency to render the slag pasty and clog a furnace with titanium deposits if it is not made by a judicious treatment to *pass into the slag*.

4°. With proper care and with fluxes very little different from those ordinarily used, ores more highly titaniferous have been smelted cleanly and profitably, but perhaps less economically than others.

5°. With a judicious adaptation of the fluxes to the composition of the ores, with a view to obtaining a slag of a certain character and to the production of special grades of pig metal adapted to the given circumstances, lean ores containing 40 and 48% of titanic acid have been successfully smelted in a regular manner for years, but at a much greater expenditure of combustibles.

6°. To decide *what* are the limits at which an ore containing titanic acid would require a modification in the ordinary charges used with similar ores free from it, would demand direct experiments, continued for a length of time, experiments which have only been made exceptionally in this country, so far as we know. How much would the extra expenditure of combustible, if any, be compensated by the special qualities claimed for the pig metal obtained, and we may say, certain to be obtained (independently of *any particular beneficial action of titanium*) by the possibility of using cheap and rich ores comparatively free from phosphorus, and, to a great extent, from sulphur; these are questions of practice on which we may have an opinion, but which cannot be discussed in this present paper, our aim having been especially to present facts upon both sides and not merely a personal theory.

7°. It cannot be maintained, at any rate, in presence of the European practice, and even of the limited American practice with such ores, that *inappreciable quantities, mere traces, or very small proportions* of titanium in ores are objectionable and sure to cause trouble in the furnace.

8°. If we rely entirely upon European practice the *metallurgy of all kinds* of titaniferous ores has been a complete success.

9°. The titaniferous ores appear to be "*par excellence*" Bessemer ores, containing little or no phosphorus, and they form, both in Europe and in many States of the Union and Canada, enormous deposits now useless.

10°. The development of the steel industry is now taxing to their limit of production the best ores of this country; at least

those available in the Eastern and Middle States. Many furnaces import hematites from Lake Superior, which cost them at the furnace from \$6 to \$7 per ton, because these ores are comparatively free from phosphorus, while nearer at hand they have titaniferous ores as rich in iron or richer and yet more free from phosphorus, but which they do not dare to work.

Even in Colorado, ores free from titanitic acid are shipped, at a great cost, to certain works which do not care to treat the immense banks of titaniferous ores near by.

The question of the use or of the exclusion of such ores is one which ought to attract the serious attention of metallurgists in this country. Enough has been done elsewhere to encourage efforts in this direction; the metallurgy of titaniferous ores is no secret. The results, if favorable, and there are all reasons to believe that they would be if we trust to what has been done in Europe, would richly pay for the expense incurred.

New York, March, 1890.

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## ABSTRACTS.

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### ANALYTICAL CHEMISTRY.

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#### Analysis of Chrome Iron. R. FRESENIUS and E. HINTZ.

The authors effect the solution of chrome iron by subjecting it, while heated, to a current of dry chlorine gas. About 5 grms. of the chrome iron are placed in a small porcelain boat and then inserted into a refractory glass tube of about 60 cm. length. Suitable safety tubes containing water are attached to collect the volatilized chlorides. The porcelain boat must be heated very gradually, and the heat, finally, is so regulated that but little of the ferric chloride reaches the first safety tube. The operation requires about 3 to 4 hours. For details as to the method for the complete analysis of chrome iron, see the original article. (*Ztschr. anal. Chem.*, 29, 28-35.)

J. F. G.

**Separation of Barium from Strontium.** R. FRESSENIUS.

The author, in a series of test experiments upon the separation of barium and strontium from one another, finds that the methods depending upon the treatment of the mixed sulphates of barium and strontium with solutions of ammonium carbonate or potassium carbonate, either with or without the presence of a soluble sulphate, are unreliable. Although separately the barium sulphate is not appreciably affected by a solution of ammonium carbonate, yet in mixture with strontium sulphate it is partly changed to carbonate when the strontium is largely in excess. When the barium is largely in excess, it prevents the decomposition of the strontium sulphate. (*Ztschr. anal. Chem.*, **29**, 20-28.)

J. F. G.

**Butter Fat.** ST. BONDZYNSKI and H. RUFI.

The authors, as a result of their researches, confirm the reports of others, that fresh butter fat may contain free insoluble fatty acids, and that the rancidity of butter is due principally to the separation of free insoluble fatty acids and not to the volatile acids, since the latter first appear in the more advanced stages of the rancidity. (*Ztschr. anal. Chem.*, **29**, 1-6.)

J. F. G.

**Examination of Alcohol.** H. BORNTÄGER.

In testing for such impurities of alcohol as aldehyde, acetal, and amyl alcohol, the author recommends the following tests:

I.—(a.) Dilute some of the sample with a large quantity of water. If oily drops separate, test these for acetal, by (6), and for amyl alcohol, by (7), as indicated below.

(b.) Test another portion for aldehyde by (8) and (3).

II.—If drops do not separate on dilution with water.

(a.) Test for aldehyde.

(b.) Dilute some of the alcohol with two volumes of water, add chloroform, mix thoroughly, and after separation, evaporate the chloroform at a low temperature and test the residue for acetal and amyl alcohol as indicated below.

If concentrated sulphuric acid and K OH produce no discoloration, only insignificant quantities of the above three impurities can be present.

- (1.)
- |                  |   |   |  |
|------------------|---|---|--|
| Chloroform ..... | $\left\{ \begin{array}{l} \text{Aldehyde is taken up, increasing the volume of the separated chloroform layer.*} \end{array} \right.$ | $\left\{ \begin{array}{l} \text{Acetal, do*} \end{array} \right.$ | $\left\{ \begin{array}{l} \text{Amyl alcohol, ditto.} \end{array} \right.$ |
|                  |   |   |  |
- (2.)
- |   |   |   |   |
|---|---|---|---|
| Ammon. Silver Sol. and water on warming ..... | $\left\{ \begin{array}{l} \text{Silver mirror} \end{array} \right.$ | $\left\{ \begin{array}{l} \text{No mirror but traces of reduction} \end{array} \right.$ | $\left\{ \begin{array}{l} \text{No reduction.} \end{array} \right.$ |
|   |   |   |   |
- (3.)
- |  |  |  |   |
|--|--|--|---|
| Colorless, aqueous sol. of fuchsin and NaH SO <sub>3</sub> ..... | $\left\{ \begin{array}{l} \text{Strong violet color changed to blue* by conc. HCl (Detects 1:500.-000)} \end{array} \right.$ | $\left\{ \begin{array}{l} \text{No color} \end{array} \right.$ | $\left\{ \begin{array}{l} \text{No color.} \end{array} \right.$ |
|  |  |  |   |
- (4.)
- |   |   |   |  |
|---|---|---|--|
| Addition of an equal volume of conc. H <sub>2</sub> SO <sub>4</sub> ..... | $\left\{ \begin{array}{l} \text{Turns brown} \end{array} \right.$ | $\left\{ \begin{array}{l} \text{Ditto} \end{array} \right.$ | $\left\{ \begin{array}{l} \text{Ditto.} \end{array} \right.$ |
|   |   |   |  |
- (5.)
- |  |  |   |  |
|--|--|---|--|
| Add an equal vol. of solution of KOH (1:3) ..... | $\left\{ \begin{array}{l} \text{Yellow color} \end{array} \right.$ | $\left\{ \begin{array}{l} \text{Ditto} \end{array} \right.$ | $\left\{ \begin{array}{l} \text{Ditto.} \end{array} \right.$ |
|  |  |   |  |
- (6.)
- |   |   |  |  |
|---|---|--|--|
| Add equal vol. of conc. H <sub>2</sub> SO <sub>4</sub> and then KOH ..... | $\left\{ \begin{array}{l} \text{Carbonized and faint smell of acrolein*} \end{array} \right.$ | $\left\{ \begin{array}{l} \text{Strong odor of acrolein*} \end{array} \right.$ | $\left\{ \begin{array}{l} \text{Colored sol. of agreeable odor.*} \end{array} \right.$ |
|   |   |  |  |
- (7.)
- |  |  |  |  |
|--|--|--|--|
| Add 3 drops conc. HCl and 10 drops colorless aniline oil. .... | $\left\{ \begin{array}{l} \text{Yellowish red color if much aldehyde} \end{array} \right.$ | $\left\{ \begin{array}{l} \text{No color} \end{array} \right.$ | $\left\{ \begin{array}{l} \text{Raspberry red color.} \end{array} \right.$ |
|  |  |  |  |
- (8.)
- |                            |   |  |   |
|----------------------------|---|--|---|
| Add conc. sol. of KI ..... | $\left\{ \begin{array}{l} \text{Brown discoloration} \end{array} \right.$ | $\left\{ \begin{array}{l} \text{No color} \end{array} \right.$ | $\left\{ \begin{array}{l} \text{No color.} \end{array} \right.$ |
|                            |   |  |   |
- (*Ztschr. anal. Chem.*, 28, 60-62.) J. F. G.

**Examination of Alcohol.** By H. BORNTÄGER.

In continuation of the above (*Ztschr. anal. Chem.*, 60) the author points out the following characteristics of propyl alcohol, C<sub>3</sub>H<sub>8</sub>O,

\* The author's own observation.

and the butyl alcohol of fermentation,  $C_4H_9OH$ , both of which may occur in crude alcohol :

	Normal Propyl Alcohol.	Fermentation Butyl Alcohol.
1. Sp. Gr.....	0.813	0.805.
2. Boiling point.....	97° C	108-109° C.
3. Solubility in Water..	Easily.....	With difficulty.
4. Odor when rubbed on the hand.....	A g r e e a b l e, fruity odor -	Disagreeable, oily odor, suggestive of fusel oil.
5. Add chloroform to the alcoholic sol. 30%		Taken up by the chloroform.
6. Reaction of 10 c. c. of the alcoholic sol. with 3 drops of conc. HCl and 10 drops aniline oil .....	Raspberry red color (if the imp. is present in large quantity).	

Hence if a 30% crude alcohol is shaken with chloroform, the latter will contain, after separation, the amyl alcohol, acetal, aldehyde, and butyl alcohol of fermentation while ethyl alcohol, acetic acid and propyl alcohol will remain in the supernatant liquid. (*Ztschr. anal. Chem.*, 28, 670.) J. F. G.

#### Estimation of Quinine in Quinine Tannate. SIGMUND NEUMANN.

The author in examining quinine tannates by Orrillard's method found the method extremely unreliable, and, therefore, resorted to the following process :

2 grms. of the finely pulverized quinine tannate were added to 20-25 c. c. of KOH solution (sp. gr. 1.240) contained in a glass stoppered cylinder of about 300 c. c. capacity. The mixture was thoroughly shaken, diluted with water to 60-80 c. c., 100 c. c of ether added and the whole again shaken. After separation of the ether, an aliquot\* part of the latter was taken for evaporation and the quinine calculated from the residue. Quinine tannate should contain from 25-30% of quinine. (*Ztschr. anal. Chem.*, 28, 663-668.) J. F. G.

\*More accurate results would be obtained by exhausting the alkaline solution with chloroform or ether and taking the whole of the solvent used, which would prevent the errors due to change in volume of the ether through evaporation or change in temperature. J. F. G.

**Abstracts of American Patents Relating to Chemistry.**

(From the U. S. Patent Office Gazette.)

*Issued March 18th, 1890.*

**423,408.**—Centrifugal machine. D. H. Benjamin.

**423,480.**—Filter. O. H. Jewell.

**423,479.**—Composition for felting boots, etc. A. D. Kizer.

Consists of alum, oil of vitriol and water.

**423,516.**—Apparatus for manufacturing oil gas. H. H. Engleman.

**423,522.**—Lubricant. J. Lewandowski.

Consists of prussiate of potash, sulphur and oil.

**423,530.**—Disinfectant. J. M. Raymond.

Consists of zinc acetate, boric acid, aluminium sulphate and acetate, sodium hyposulphite, mercuric iodide and acetic acid.

**423,550.**—Process of making blue dyes. C. Duisberg.

A blue coloring matter that will dye cotton in an unmordanted bath, and wool in a neutral bath is obtained by combining the tetrazo-compound of benzidine disulphonò-disulpho acid, with alpha or beta naphthylamine, or their alkyl derivatives.

**423,569.**—Azo dye. P. Ott.

The process of obtaining substantive dyestuffs from intermediate products not dyestuffs in themselves, derived from diamidodiphenylene oxide and from diamidoditoluylene oxide, which consists in combining the tetrazo compound of the latter with one molecule of an amine or a phenol, or their sulpho or carbo or their sulpho-carbo acids, and combining the product of the reaction with another molecule of an amine or a phenol, or their sulpho or carbo acids or their sulpho-carbo acids.

**423,583.**—Fire and waterproof roof covering. J. G. Wolf.

Is composed of fine particles of woody material, burnt magnesite and magnesium chloride.

**423,615.**—Filter. W. Mailler.

**423,656.**—Paint. C. L. Baker and M. Thorkelson.

Consists of raw linseed oil, lamp black, coach japan, turpentine and natural mineral paint.

**423,683.**—Acid bottle. E. Hart.

The bottle is constructed of mineral and animal wax, and provided with a stopper of the same material.

**423,699.**—Roofing composition. M. W. Powell.

Consists of resin, asphaltum, petroleum residuum, kidney oil and actinolite.

**423,767.**—Filter. W. M. Hough.

**423,768.**—Air pumping apparatus. S. E. Hughes.



**423,866.**—Soap. J. A. Gunn.

A hard soap having animal hair in appreciable and interlocking and intertwining lengths combined therewith.

**423,868.**—Production of chlorine gas. C. Hornbostel.

**423,869.**—Apparatus for making fluid extracts. J. W. Hyatt.

**423,875.**—Disinfectant. D. W. Macdonald and J. G. Flower.

Consists of boric acid and salicylic acid in combination with potassium permanganate and a silicate.

**423,883.**—Disinfectant. W. P. Taggart.

Consists of chloride of lime, water, potassium permanganate, salt and saltpetre.

*Issued March 25th, 1890.*

**423,896.**—Laboratory burner, specially useful with gasoline gas. J. F. Barker.

**423,898.**—Air carburetor. R. D. Bradley.

**423,927.**—Soap powder. H. Hayward.

A mixture of ammonium chloride, borax, sodium carbonate, and soap not melted, but ground together in a cold and dry state.

**423,930.**—Process of diffusion for sorghum cane, etc. H. A. Hughes.

**423,949.**—Process of purifying brine. C. C. Peck.

The brine is treated with sodium carbonate at its boiling point.

**423,970.**—Blue carbon dye. M. Ulrich.

The process of obtaining substantive dyestuffs from intermediary products that are not dyestuffs, which consists in combining one molecule of a paradiamine with one molecule of a dioxynaphthaline sulpho acid, and then combining one molecule of the intermediary product obtained with another molecule of dioxynaphthaline sulpho acid.

**423,978.**—Bottle stopper. E. W. Abbe.

**423,995.**—Wire galvanizing apparatus. B. A. Grant.

**424,005.**—Ice machine. J. C. Kitton.

**424,019.**—Brown carbon dye. R. Nielzki.

Yellowish brown coloring matter of the formula  $C_n H_{2n-8} (NO_2)_N$ ,  $C_n H_{2n-9} (OH) (COOH)$  produced by condensing a nitro-diazo body with an ortho-oxycarbonic acid, insoluble in water and dilute acids, readily soluble in alcohol, ether and diluted alkalies.

**424,024.**—Blowpipe. W. R. Rawlings and J. J. Rawlings.

**424,080.**—Transparent filler. J. A. Skerry and J. Derosier.

Consists of oil, turpentine, drier and lime.

**424,124.**—Apparatus for purifying water. F. H. Moore.

**424,228.**—Method of applying designs to watch dials. F. Schmalz and J. C. Firmbach.

The process consists in covering the face of the dial with a soluble sensitive coating, which becomes insoluble on exposure to light, exposing the

dial to light under a negative, then applying a liquid enamel or ink over the whole surface, covering both the exposed and unexposed portions, then washing off the portions of the coating remaining soluble, and finally firing the dial to set the remaining portions of the enamel coating.

**424,252.**—Composition for ornamental brick. J. C. Anderson.

A mixture of clay and brass.

**424,253.**—Composition for ornamental brick. J. C. Anderson.

A mixture of clay and copper.

**424,254.**—Composition for ornamental brick. J. C. Anderson.

A mixture of clay and phosphor bronze.

**424,299.**—Combustible coal brick. J. H. Hiertz.

Consists of coal dust or slack, slaked lime, tar, salt and turpentine.

**424,303.**—Filtering apparatus. H. J. E. Jenson.

**424,325.**—Apparatus for mixing and aerating wort and yeast. J. Meier.

**424,328.**—Composition for fireproof paper or board. J. G. Merrill.

Consists of vegetable or animal fiber, asbestos, alum or copperas, a coloring matter, infusorial earth, and sodium silicate.

**424,352.**—Process of producing marble-like or enamel-like objects. L. Preussner.

Consists of basic magnesium chloride and a filler.

**424,353.**—Process of producing artificial stone. L. Preussner.

Burnt magnesia of commerce is mixed with concentrated hydrochloric and boric acid, in proportions to produce a basic magnesium chloride and magnesium borate, and the product is mixed with a filling material.

**424,357.**—Pepsin. J. B. Russel.

Is obtained by macerating hogs' stomachs, clarifying the resulting solution, subjecting the solution to dialysis, and evaporating the remaining solution.

**424,375.**—Filtering apparatus. T. Stewart.

*Issued April 1st, 1890.*

**424,464.**—Filtering machine. J. A. Crocker.

**424,547.**—Plaster. J. E. Turner.

Consists of sand, plaster of paris, prepared slag, glue and alum.

**424,590.**—Candle for killing insects. R. Atkinson.

Consists of stearin or other equivalent material mixed with insect powder and alum, and molded around a wick.

**426,615.**—Apparatus for refining camphor. W. V. McKenzie.

**426,653.**—Paint. R. Morris.

Consists of about 20 parts resin, and 7 parts each of zinc oxide and gypsum, powdered and mixed together and adapted to be either fused by heat upon the surface to be protected or to be liquefied by a solvent.

**424,679.**—Filter. F. Lascar.

**424,755.**—Furnace for recovering soda. H. Blackman.

**424,756.**—Process of recovering soda. H. Blackman.

**426,760.**—Apparatus for drying starch or other solid matter. F. M. F. Cazin.

**426,762.**—Filter. W. D. Cummings.

*Issued April 8th, 1890.*

**424,961.**—Composition for treating fuel. J. C. Cooper.

Consists of sodium chloride, aluminium sulphate and potassium carbonate.

**424,991.**—Simultaneous manufacture of soaps and carbonic acid. E. D. Mellen.

An alkaline carbonate or bicarbonate is mixed with rosin or any suitable organic acid in a digester provided with suitable means both for regulating the chemical action and for withdrawing the gas, and spraying the mixture with fine jets of steam.

**425,089.**—Chloral formamide. J. F. von Mering.

**425,040.**—Chloral formamide. J. F. von Mering.

Prepared by treating chloral with formamide.

**425,081.**—Process of making zinc sulphide. A. Keiller.

To a solution of a zinc salt is added an alkaline sulphate and hydrothionic acid.

**425,246.**—Bunsen gas burner. L. Paget.

**425,292.**—Apparatus for manufacturing oxides of metals. S. R. Bradley and A. C. Bradley.

**425,310.**—Apparatus for the pasteurization of beer. T. Evans.

**425,316.**—Process of distilling water. A. Gerdes and B. Thoens.

**425,350.**—Method of and apparatus for manufacturing artificial fuel. G. Y. Smith.

**425,351.**—Artificial fuel. G. Y. Smith.

Consists of peat, 1,200 parts; culm, 600 parts; rosin, 100 parts; pitch, 100 parts; rye flour, 5 parts, and lime, 5 parts.

**425,374.**—Filter. C. B. Elliott.

W. R.

*Issued April 15th, 1890.*

**425,412.**—Composition for coating iron and wood. I. T. Dyer.

Consists of asphaltum, sulphur, lamp-black and lard oil.

**425,418.**—Welding compound. M. Garrison.

Consists of borax, carbonate of iron, clay, and small particles of iron filings.

**425,421.**—Apparatus for treating beer. C. Haefner.

An apparatus for forcing the carbon dioxide produced by fermentation into the casks of beer.

**425,431.**—Filter of porous fabric. J. W. Hyatt.

**425,504.**—Red dye. R. Gnehm.

Obtained from succinic acid and dimethylmeta-amidophenol.

**425,525.**—Orthonitroparadiamidodiphenyl. J. Schmid.

**425,537.**—Water filter. C. H. Dismitt and G. W. Walters.

**425,545.**—Apparatus for saving gold, silver and quicksilver. F. A. Luckenbach.

**425,578.**—Filter. O. H. Jewell and W. M. Jewell.

**425,608.**—Process of treating kitchen garbage. G. Fleischman.

The garbage is converted into a dry fertilizer and grease, by drying and extracting with a volatile solvent.

**425,614.**—Dyeing apparatus. C. L. Klander.

**425,648.**—Gelatinous explosive. F. A. Abel.

Consists of nitroglycerin and nitrocellulose to which tannin is added, whereby the explosive is rendered of a propulsive instead of a disruptive character.

**425,661.**—Process of galvanizing plates. E. A. Davies.

**425,668.**—Compound for cleaning jewelry. F. Graffe, Jr.

Consists of potassium bitartrate, rouge, potassium hydroxide and water.

**425,675.**—Means for coating metal pipes. J. D. Hooker.

Metallic pipes are coated inside and outside with the gummy residuum produced in the distillation of some petroleums, and known as "purified maltha."

**425,708.**—Dye vat. C. A. G. Schmidt.

**425,818.**—Apparatus for the reduction of argentiferous ores. O. Lumaghi.

**427,877.**—Process of carbureting air or gas. S. Hanford.

**425,885.**—Process of making azo dyes. M. Kohn.

The process of producing violet to blue-black azo dyes for dyeing wool, which consists in combining the diazo compounds of the sulpho acid of aniline or its specified equivalents with alpha-naphthylamine, again diazotizing the amidoazo compounds thus obtained, and combining therewith phenylalphanaphthylamine or a homologue thereof.

**425,869.**—Art of reclaiming rubber from waste rubber stock. N. C. Mitchell.

**425,904.**—Composition for preserving food. W. Radam.

A fumigating composition consisting of sulphur, sodium nitrate, manganese dioxide, sandalwood, and potassium chlorate.

**425,905.**—Process of utilizing acid for residuums. C. Rave.

**425,919.**—Dye for leather. E. O. Wallace and S. M. Wallace.

Consists of ferrous sulphate, aniline, potassium bichromate and cupric sulphate.

W. R.



REGULAR MEETING, MAY 2, 1890.

Vice-President Breneman in the chair. The minutes of the last meeting were read and accepted.

Dr. Wm. McMurtrie, N. Y. Tartar Co., 83 William street, was elected to membership, and Lt. W. R. Quinan, of Cal. Powder Wks., Pinola P. O., Cal., was elected to Associate membership.

The following applications were received: Chas. A. Catlin, Rumford Chemical Works, Providence, R. I., as a member; D. F. Lucas, M.D., Brooklyn, N. Y., as an Associate member.

The subject of the revision of the Constitution was then presented for discussion. The Chair stated that the full text of the proposed new Constitution still lacked a few sections to be passed upon by the Board of Directors before presentation to the Society, and suggested that a meeting be called within two weeks at which the amendments proposed could be presented for full discussion, that they be then printed and sent to out of town members so that the vote could be taken at the June meeting.

A lengthy discussion took place upon the interpretation of the article in the present Constitution on the subject of amendments.

Dr. Hale held that under this article the Society has no authority or power to modify amendments originated and presented by the Board of Directors. Mr. Wainwright held to the contrary, and, the Chair being called upon, ruled that the Society had no such right, that the amendments must be passed upon by the Board of Directors and then presented to the Society. The Chair was sustained in this ruling by a vote of nine to two, two members not voting.

It was then moved that the Society meet again on May 16 to consider the amendments as officially presented. Seconded and carried.

Mr. Wainwright moved that the session be resolved into a Committee of the Whole to recommend its wishes upon the subject of revision to the Board of Directors. Seconded and carried. The chairman of the meeting was made chairman of the Committee of the Whole. The proposed Constitution was then read section by section and discussed.

It was then moved that Committee of the Whole arise. Carried. The meeting was then adjourned.

CHAS. F. MCKENNA,

*Recording Secretary.*

## EUGÈNE MELCHIOR PÉLIGOT.

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Eugène Melchior Péligot was born in Paris, February 24th, 1811, and died in that city on the 15th of April last in his seventy-ninth year.

The death of Péligot is a severe blow to science, which loses in him an unpretentious master and an indefatigable worker.

His life was devoted to the teaching of chemistry. As a lecturer he was noted for the perfection of his method, the clearness of his exposition, the largeness of his views, and the simplicity of his diction.

After completing his studies at the College of Henry the Fourth, he entered as "*élève ingénieur*" at the *Ecole Centrale des Arts et Manufactures*, in 1829.

The influence of the incomparable lectures of Dumas, then professor of chemistry at that school, was soon felt by Péligot, whose calling from that date was irrevocable. He devoted himself to the study of chemistry and had hardly left the school when Dumas, who had appreciated his capacity, admitted him to his laboratory.

His first researches comprised the study of the compounds of chromium.

He discovered and described the monoxide of this element and its sulphate, oxalate and chloride, the dioxide of chromium and the dichromate of potassium chloride.

In 1834 he was appointed assistant professor of chemistry at the Ecole Centrale, and, two years later, being only 25 years old, he succeeded Dumas, his illustrious master, and occupied this position until 1873.

In 1835 Dumas chose him as collaborator in the brilliant researches which they made in common on methylic alcohol and its principal derivatives, one of the most remarkable achievements of the time in organic chemistry. This was soon followed by the

description of ethalic ether, sulphacetic acid, cetyl chloride and by researches of Pélégot alone on the benzoates.

In 1838 he prepared monobrombenzoic acid by the action of bromine upon silver benzoate.

As early as 1789 Klaproth had discovered "uran" in pitchblende. This body was examined by Arfvedson and Berzelius and later by Ebelmen and Pélégot.

In 1823 Arfvedson thought that he had isolated a metal by acting with hydrogen upon the green oxide of uranium, but in 1840 Pélégot demonstrated that "uran," which until that time had been considered as an element, was in reality a compound of oxygen with a metal which he isolated and called uranium. This important discovery was followed by an exhaustive study of the salts of uranium and their molecular constitution.

In 1845, being "répétiteur" at the Ecole Polytechnique, he was chosen as commissioner by the Chamber of Commerce of Paris to the Exposition of Industrial Products at Vienna, and on his return was appointed professor of chemistry at the *Conservatoire des Arts et Métiers* and *chief assayer* at the Mint.

In 1852 he was elected member of the Academy of Sciences. From that time Pélégot devoted himself to the study of applied chemistry.

His researches on the analysis of natural waters, as fertilizers, and on the disease of the silk worms, are printed in the *Mémoires de l'Académie*.

His works on the combination of ordinary sugar with bases, and especially with lime and baryta, have established on a firm basis the theory of the extraction of sugar from beet juice and from its residues, molasses, and have been of the greatest importance to one of the most extensive European industries.

He thoroughly studied and gave the theory of the manufacture of glass. He demonstrated that glass must be composed of a mixture of silicates in indefinite proportions to prevent crystallization, which renders the glass very brittle. He obtained dichroic glass by introducing oxide of uranium into the mixture of silicates.

He pointed out that an excess of alkalies in the composition of



glass, and particularly in bottle glass destined to contain wines, was to be avoided.

The celebrated antique vase known as the "Portland Vase," now in the British Museum, had been thought to be an early example of ceramic art until Pélégot, examining it critically, discovered it to be an ancient specimen of glass manufacture.

His lectures at the Ecole Centrale are well remembered by the numerous engineers and chemists who, like the writer, had the good fortune to follow them. They heard the master with the deep respect that a profound knowledge of science commands.

In April, 1854, he was made "*Chevalier de la Légion d'Honneur*," "*Officier*" in 1857, "*Commandeur*" in 1878, and "*Grand Officier*" in 1885.

In 1873 Pélégot, then member of the Institute, Secretary of the Society for the Advancement of Sciences, since 1836, member of the "*Conseil d'hygiène et de Salubrité*" (Board of Health), professor at the "*Conservatoire des Arts and Métiers*," and at the "*Institut Agromanique*" and Director of the assays at the Mint, felt that his health was failing and gradually retired from active work.

The following are his principal publications :

*Traité élémentaire de manipulations chimiques.* 1836.

*Recherches sur la nature et les propriétés chimiques des sucres.* 1838.

*Recherches sur l'analyse et la composition chimique de la betterave à sucre.* 1839.

*Rapport sur les expériences relatives à la fabrication du sucre et à la composition de la canne à sucre.* 1842.

He edited the *Traité d'analyse chimique de H. Rose*, in 1843.

*Rapport sur les produits exposés à Vienne, en 1845.* 1846.

*Le Verre, son histoire et la fabrication*, in 1875.

AUGUSTE J. ROSSI,

*Ingenieur de l'Ecole Centrale des Arts et Manufactures.*

## NOTES ON QUANTITATIVE ANALYSIS.

BY L. H. FRIEDBURG, Ph. D.

The following chapters make but little claim to originality, and treat only of well known facts. But as every chemist during a long period of analytical occupation develops for himself a particular *modus operandi*, based upon results obtained, it is proper to recommend what he deems to be valuable. In this sense I offer the descriptions given below, omitting all reference to literature or authorship of the different methods; premising only that not *one* is described that I have not myself frequently used.

### A. ACIDIMETRY AND ALKALIMETRY.

The test liquids used are hydrochloric acid and ammonium hydrate. It is customary to prepare normal or deci-normal solutions. With solids, provided they are pure, this may be arrived at to a degree of accuracy practically sufficient. With solutions of gases such as HCl or  $\text{NH}_3$ , the preparation of a normal solution, even if performed with the greatest care and the best, standardized measuring vessels or specific gravity apparatus, we cannot omit quantitative determination of at least *one* of the liquids prepared. The following figures will show that in trying to prepare normal solutions of the aforesaid liquids a difference of 0.1957 per cent. of HCl and of 0.0740 per cent. of nitrogen were quantitatively determined. For very accurate work such determination ought to be made and no attempt to normalize afterwards by dilution or concentration is necessary or desirable. The measuring of new quantities of liquids is a source of new errors at best. The sacrifice of the advantage of rapid final calculation of results with such solutions is well balanced by greater accuracy obtained.

900 c. c. hydrochloric acid *puriss.*, Sp. Gr. 1.20, were mixed with about 8000 c. c. of distilled water, while 450 c. c. of the commercially pure, strong ammonium hydrate were added to about 6400 c. c. of dist. water. The mixtures were allowed to

stand for a week. Then it was ascertained how these two liquids would neutralize each other by volume. The whole length of the burettes was used, and in the last determination they were filled up again. It was found, using cochineal as an indicator, that :

- a. 20 c. c. H Cl were neutralized by 25 c. c.  $\text{N H}_4 \text{ O H}$ .
  - b. 20 c. c. H Cl were neutralized by 25 c. c.  $\text{N H}_4 \text{ O H}$ .
  - c. 20 c. c. H Cl were neutralized by 24.95 c. c.  $\text{N H}_4 \text{ O H}$ .
- 20 c. c. H Cl therefore corresponded to 25 c. c.  $\text{N H}_4 \text{ O H}$ .

Next, three different weighed quantities of H Cl were taken and neutralized (using the same indicator) with ammonia. The results were:

- a. 19.7861 grms. H Cl required 24.30 c. c.  $\text{N H}_4 \text{ O H}$ ,  
consequently 1 gram. H Cl required 1,228 c. c.  $\text{N H}_4 \text{ O H}$ .
  - b. 5.8800 grms. H Cl required 7.20 c. c.  $\text{N H}_4 \text{ O H}$   
therefore 1 gram. H Cl required 1,224 c. c.  $\text{N H}_4 \text{ O H}$ .
  - c. 15.4551 grms. H Cl required 19.00 c. c.  $\text{N H}_4 \text{ O H}$ ,  
or, 1 gram. H Cl required 1,229 c. c.  $\text{N H}_4 \text{ O H}$ .
- 1 gram. H Cl, therefore, was neutralized by 1.23 c. c.  $\text{N H}_4 \text{ O H}$ .

Finally, three chlorine determinations were made. The silver chloride was dried as usual, but only that part of it which would spontaneously leave the filter when emptied into the porcelain crucible was determined as horn silver, the filter and the remaining amount were burned in a weighed platinum spiral until the silver was reduced to a metallic state, adhering as a little knob to the wire, which was again weighed. Following are the results:

- a. 9.9710 grms. H Cl gave 1.66603 grms. Ag Cl equal to 0.42362 H Cl.
- b. 1.8240 grms. H Cl gave 0.3023 grms. Ag Cl equal to 0.0769 H Cl.
- c. 7.8802 grms. H Cl gave 1.31663 grms. Ag Cl equal to 0.33478 H Cl.

From these analyses the following amounts of H Cl in one gram. of the liquid were calculated:

- a. 1 gram. H Cl contains 0.04249 gram. H Cl gas.
- b. 1 gram. H Cl contains 0.04218 gram. H Cl gas.
- c. 1 gram. H Cl contains 0.042485 gram. H Cl gas.

A noticeable loss having occurred in the determination b, the

average of *a* and *c* was taken; 1 grm. H Cl contains .04249 gaseous H Cl. The difference between the average taken from all three determinations, and of that from the two mentioned, however, is only 0.0001 grm.

From all the above it follows that :

1 grm. H Cl solution is neutralized by=1.23 c.c.  $\text{NH}_4\text{OH}$  solution.

1 grm. H Cl solution contains=0.04249 gr. H Cl gas.

1 c.c.  $\text{NH}_4\text{OH}$  solution contains=0.013264 grm. nitrogen.

1 c.c.  $\text{NH}_4\text{OH}$  solution is neutralized by=0.8 c.c. H Cl solution.

1 c.c. H Cl solution contains=0.034543 grm. H Cl gas.

or=0.033596 grm. chlorine.

These solutions were prepared in February, 1888. The H Cl solution was kept in a large flask with doubly perforated rubber stopper, one hole of which allowed the escape of the liquid by means of a syphon (or self feeding burette) while the second opening was connected with a small flask containing a few c. c. of the same liquid as the large one. The ammonia bottle was closed with a doubly perforated *cork*. A small flask, containing a little liquid of the same strength, a second small flask which is kept empty and finally a cylinder, containing cotton, solid KOH and again cotton, are attached, in the above sequence, to one opening, the other serving for the outlet of the liquid.

These liquids are kept standing in the laboratory, not exposed to direct sunlight, but subject to the natural variations of temperature during the year. Nevertheless, they have not changed during these last *two years* under the given conditions. To-day, as two years ago, 20 c.c. of the H Cl solution is saturated by 25 c. c. of the ammonia solution, while both solutions, when used in a nitrogen determination of urea which had been six times recrystallized and finally dried over sulphuric acid, then heated with soda lime, was shown to have retained the previously determined percentage, the urea analysis yielding figures of *absolute* correctness.

## B. ANALYSIS OF INSOLUBLE SILICATES, MAINLY PORPHYRIES, ETC. \*

A quantity sufficient for eight different assays is crushed, powdered and sifted through fine muslin. No pressure should be used while dusting, but the muslin which covers a jar and carries the powder is covered by a piece of chamois, and both pieces are tied around the neck of the dry jar. The chamois is then gently tapped with the fingers.

### FIRST PORTION.

$\text{SiO}_2$ ; Fe; Al; (Mn); Ca; Mg.

The powder is mixed in a platinum crucible with eight times its weight of absolutely dry powdered sodium carbonate. The crucible is covered and then heated with the blast lamp. At the beginning of this operation the sleeve at the mouth of the blow pipe is drawn so far forward that an agitated, blue flame results. The effect is, that the entire crucible (cover and all), become at once red hot, thus avoiding any decrepitation inside. After a time the sleeve is pushed back, allowing the ordinary flame to play. This is continued for about fifteen minutes, until the mass flows without bubbles. Then the crucible is suddenly cooled by turning off the gas and blowing the cold air from the bellows against it. The cake will subsequently fall out easily, without the necessity of pressing or distorting the crucible. If the fused mass looks merely greenish, this indicates only traces of sodium manganate, but if more intense coloration is visible the presence of manganese must be taken into account in the course of the analysis. The cake is put into a separate beaker, containing a little water, the crucible and cover are put into another beaker. Both beakers receive a gradual addition of HCl and are gently heated. After all is dissolved, except gelatinous  $\text{SiO}_2$ , the heating is continued until no more  $\text{CO}_2$  is present. The combined liquids from the two beakers are then transferred to a platinum dish and evaporated to dryness on the water bath. The lumps of gelatinous  $\text{SiO}_2$  must be frequently crushed so that they cannot enclose soluble silicic acid. The residue is moistened with a few drops of conc. HCl, then diluted with

\* This process with few changes was commonly used in Bunsen's laboratory. L. H. F.

water and filtered with the pump. The filter with  $\text{SiO}_2$  is (after complete washing) put while moist into a platinum crucible, heated and weighed until the weight is constant. The silicic acid is then treated with HF (free from all residue), and a few drops of  $\text{H}_2\text{SO}_4$  upon the water bath, until all volatile matter is driven off; the residual  $\text{H}_2\text{SO}_4$  is expelled over a free flame, the residue, if any, is heated to redness and weighed. The treatment with HF and  $\text{H}_2\text{SO}_4$  may be repeated if necessary. In case the residue should be considerable it must be quantitatively tested for Al, Fe, Ca and Mg, otherwise a qualitative test is sufficient.

The filtrate from the  $\text{SiO}_2$  determination is heated and oxidized by a few drops of  $\text{HNO}_3$ , after which Fe and Al are precipitated with a very slight excess of  $\text{NH}_4\text{OH}$ , and the unavoidable excess of this latter is boiled off immediately. Care should be taken not to expose this liquid too long to the air. It would attract  $\text{CO}_2$  and precipitate Ca. If an interruption is unavoidable, the beaker must be placed upon a dish containing a layer of  $\text{NH}_4\text{OH}$  and a larger beaker must be inverted over the smaller one, its edge immersed in the layer. The precipitate consists of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ , with small traces of  $\text{SiO}_2$ , Ca and Mg.

This precipitate may be treated in two different ways, according as it is smaller or larger, especially as regards the quantity of iron present.

I.—*For small quantities of iron.* The precipitate is heated and weighed, then fluxed with potassium bisulphate in a closed crucible at low temperature, so as just to make the mass flow, cooled, dissolved in water, the iron is reduced with zinc and the solution titrated with permanganate. In case HCl was used to dissolve the reduced iron,  $\text{H}_2\text{SO}_4$  is added before titration, in excess, because the sulphate solution is lighter in color than the chloride, and also because strong dilution is desirable.

II.—*The precipitate is abundant and much iron is present.* Dissolve in HCl and digest for half an hour in a platinum dish with an excess of KOH upon the water bath. The details of manipulation are as follows: The precipitate being washed thoroughly, is, for the greatest part, brought into the platinum dish by means of a platinum spatula. The remaining portions on the

filter are dissolved in a hot mixture of equal parts of conc. HCl and  $H_2O$  by means of a pipette. The solution is allowed to run into the main precipitate in the platinum dish. The filter is washed with water, this filtrate running into a beaker. The mass in the platinum dish is then cautiously treated with KOH solution, a few pieces of solid KOH are added, digestion for half an hour upon the water bath follows, and the mass is then diluted with the wash filtrate which was collected separately in the beaker and filtered through the aforesaid filter. This filtrate contains the  $Al_2O_3$ . Acidulate with HCl, so that solution just takes place after the first precipitation, and precipitate with freshly prepared ammonium sulphide. This latter is used in preference to ammonium hydrate, because  $Al_2O_3$  is less soluble in the former; the  $(NH_4)_2S$  must be freshly prepared in order to avoid polythionic salts as well as ammonia resulting from decomposition by age.

The previously mentioned precipitate containing  $Fe_2O_3$  (and traces of  $CaO$ ,  $MgO$  and  $SiO_2$ ) is heated and weighed. Of course, the crucible during this heating must remain open, in order to avoid reduction by gases from the flame. Dissolve in conc. HCl, filter from  $SiO_2$ , reprecipitate iron with  $NH_4OH$  and add the filtrate to the liquid containing these substances.  $SiO_2$  and  $Fe_2O_3$  are to be treated as described before, and weighed separately.

Should the remaining filtrate now be too abundant it must be concentrated after acidulation with HCl. A little  $NH_4OH$  is added to precipitate remaining  $Al_2O_3$  and, if this is still present, the ammonia is driven off and the precipitate filtered, added to the first precipitate, heated and weighed as  $Al_2O_3$ .

The combined filtrates, concentrated as above, contain Mn, Ca and Mg for determination. If enough Mn were present this must first be precipitated by means of ammonium sulphide. Wash with water containing some  $(NH_4)_2S$ , redissolve in HCl, boil the solution to separate sulphur and filter. Concentrate the filtrate, precipitate with  $Na_2CO_3$ , boil in order to destroy manganese carbonate which might have formed, wash with boiling water, heat and weigh as  $Mn_3O_4$ .

Before precipitating Ca, the filtrate must be acidulated with

HCl, thus separating sulphur and then filtered. Render slightly alkaline with  $\text{NH}_4\text{OH}$  and add ammonium oxalate, boiling. Filter after twelve hours. Put the moist, well washed filter, with precipitate, into a platinum crucible, heat strongly for fifteen minutes before the blast lamp and weigh as  $\text{CaO}$ . This weight must be controlled. Redissolve the  $\text{CaO}$  in HCl, reprecipitate as above, and add the filtrate to the liquid containing Mg. Heat the  $\text{CaO}$  to constancy before the blast lamp. Test it with the spectro-scope for Ba and Sr.

Before precipitating Mg (particularly if this is present in small quantity only) drive off the ammonium salts as thoroughly as possible. Dissolve in a little HCl until the liquid is slightly acid, add sodium phosphate, then ammonium hydrate until a turbidity sets in, then a quantity of ammonium hydrate equal to one-third of the volume of the liquid; filter after four hours and wash with a mixture of one part of  $\text{NH}_4\text{OH}$  and three parts of water. Formerly, a period of twenty-four hours was deemed necessary for this precipitation, but, generally, four hours are fully sufficient. The precipitate is washed until no more chlorine is present. Now, either dry the filter with precipitate and incinerate separately, or better, especially if the pump was used for washing, bring the moist precipitate and filter into a platinum crucible. Heat gently at first, finally before the blast lamp energetically. Should the pyrophosphate prove to contain a little carbon, moisten with a few drops of  $\text{HNO}_3$ , evaporate cautiously to dryness and heat again, as above.

If the spectroscopic research proved the presence of sufficient Ba and Sr, the  $\text{CaO}$  precipitate has to be further treated. Transfer from the platinum crucible into a small, thin well tempered flask of 5 to 10 c. c. capacity. Wash the residue from the crucible with  $\text{HNO}_3$  into the flask and add more  $\text{HNO}_3$  to this latter, until all Ca is transformed into nitrate. The solution may be turbid from filter ash or from Ba or Sr salts. Evaporate over a small, direct flame to dryness, blow out the residual  $\text{HNO}_3$  vapor by means of a glass pipe, and add not more alcohol than is necessary to obtain on heating a syrupy solution of calcium nitrate. Allow to stand for twenty-four hours, filter from barium and



strontium nitrate, wash with absolute alcohol. If a sufficient quantity now remains upon the filter, dissolve this in hot water and allow the solution to run into a weighed platinum crucible. Evaporate to dryness and heat before the blast to constant weight. (BaO and SrO.) Now dissolve in conc. HCl, evaporate in the same little flask as previously used to dryness, separate  $\text{SrCl}_2$ , soluble in absolute alcohol by means of this. Precipitate  $\text{BaCl}_2$  as sulphate and weigh. Sr is found by difference. In case no weighable amount of  $\text{BaCl}_2$  should have remained after the  $\text{SrCl}_2$  was dissolved in absolute alcohol, allow the syrup of  $\text{SrCl}_2$  to be taken up by a strip of filter paper, wind around this a thin platinum wire, incinerate in an open flame, heat until the sodium flame has disappeared and then use the spectroscope, dipping the platinum wire frequently into HCl. Mere traces of Ba will only become visible after almost perfect evaporation of  $\text{SrCl}_2$ .

#### SECOND PORTION.

##### DETERMINATION OF THE ALKALIES.

The powder is put into a platinum crucible, moistened with a few drops of conc.  $\text{H}_2\text{SO}_4$  and then digested three or four times with conc. HF upon the water bath. This done, the small crucible is put upright inside of and near the bottom of a large platinum crucible lying horizontally. A small flame is applied underneath the side nearest the mouth of the large crucible and the burner is gradually pushed towards the middle and near the end. The  $\text{H}_2\text{SO}_4$  and hydrofluorsilicic acid are thus expelled. This expulsion must be performed thoroughly so that afterwards no glass vessel may be attacked by remaining HF. The small platinum crucible is not allowed to become red hot in order that alkalies may not be lost. Should the mineral not have been fully decomposed, the resulting mass must again be treated with HF on the water bath and afterwards heated, as described. Now, while the large crucible is put vertically and the small one inserted into the same, enough conc. HCl is added to dissolve all  $\text{CaSO}_4$ , and the large crucible containing the small one standing within is heated upon the water bath. Generally it is found that a residue is left. The liquid must then be decanted and the residue treated

as before. After perfect solution, the contents of the small crucible are emptied into the large one, washing carefully. Then  $\text{BaCl}_2$  and (without filtering)  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{CO}_3$  are added and the precipitate is filtered and washed and the united filtrates are evaporated to dryness. The ammonia salts are expelled by very cautious heating, so that no decrepitation may take place. The residue is dissolved in water,  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{CO}_3$  are again added, filtration, evaporation and expulsion of ammonia salts is repeated again and again, until no further precipitate is formed by addition of these reagents. It is advisable to use for every new filtration a smaller platinum dish, so as not to get too much filtrate. The final solution must be absolutely free from ammonium salts.

A small quantity of pure, red  $\text{HgO}$  is added in order to transform  $\text{MgCl}_2$  into  $\text{MgO}$  while  $\text{HgO}$  is transformed into volatile  $\text{HgCl}_2$ . The platinum dish is covered with a watch glass and digested (so that the mass is just kept moist) for two hours. An excess of water has to be avoided or else the reaction does not take place. After this dry for 1 to 2 hours on the water bath, and finally drive off the  $\text{HgCl}_2$  by heating, but not to redness. Dissolve in a minimum of water, filter into a weighed platinum crucible, add a drop of  $\text{HCl}$ , evaporate to dryness, heat so as to keep the mass just in a fused state in the *covered* crucible and then weigh. In order to obtain thus the sum of the alkaline chlorides, this heating and weighing has to be repeated to constancy. After the first weighings a new addition of  $\text{HCl}$  is advisable since (owing to organic substance from the filter) carbonates may have formed in heating.

Now dissolve in a few drops of water and add an excess of platinic chloride. (The preparation of c. p. platinic chloride will be given at the end of this chapter.) Care has to be taken that all  $\text{NaCl}$  is transformed into the double salt; no white cubes must remain visible in the precipitate, since these would be insoluble in alcohol. Evaporate to dryness on the water bath and in a *porcelain* dish. This is easily understood. In the first place the mixed chlorides of alkalis are generally dissolved and filtered after weighing, since an unavoidable residue of  $\text{Fe}$  may be present,

which must be considered ; secondly, the platinic chloride must not be evaporated in a platinum dish, as it would dissolve platinum as subchloride, which is insoluble in alcohol and would result together with potassium-platinic chloride. Allow to cool, add a few drops of water in order to dissolve the sodium double salt and throw on a filter previously washed with alcohol, dried at  $105^{\circ}$  C. and weighed. Then wash the potassium double salt first with a mixture of 1 part alcohol and 1 part water, then with 1 part water and 2 parts alcohol, finally with absolute alcohol until the filtrate runs colorless. Then wash with a mixture of 4 parts alcohol and 1 part ether. The filtrates must be preserved for the following reason : In case the determination of  $\text{MgO}$  in the filtrate should not be necessary, but that the precipitate of  $\text{K}_2\text{PtCl}_6$  should be lost, the  $\text{PtCl}_4$  would have to be reduced to metallic platinum, as described below, in order to obtain  $\text{NaCl}$ .

The precipitate is dried at  $105^{\circ}$  C. and weighed to constancy.

The filtrate is diluted with water, heated to drive off ether and alcohol and then put into a little flask with doubly perforated stopper, which carries two rectangularly bent tubes. One of these latter nearly reaches the surface of the liquid, the other ends in the neck of the flask. This second one is connected with a hydrogen apparatus. The flask is heated gently and, while still hot, the longer rectangular tube is closed outside by means of a rubber tube with glass rod. The hydrogen apparatus is now set to work, the flask cools and the hydrogen absorbed by reduction is thus replaced spontaneously. The liquid becomes colorless and platinum is dendritically separated, generally floating for some time upon the liquid, which is now filtered. If some  $\text{FeO}$  should still be present, a drop of  $\text{HNO}_3$  is added and then  $\text{NH}_4\text{OH}$ . The precipitate, if any, is filtered. Then  $\text{MgO}$  is determined and deducted as  $\text{MgCl}_2$  from the above found sum of the combined alkaline chlorides.

#### PREPARATION OF C. P. PLATINIC CHLORIDE.

The platinic chloride used in the above determination is prepared, according to Bunsen, in the following manner, which involves the separation of platinum from iridium, rhodium and palladium :

Dissolve platinum in aqua regia, taking 4 pts. HCl and 1 pt.  $\text{HNO}_3$ , adding this latter very gradually while the flask stands on the water bath. After complete solution has taken place evaporate, also on the water bath, to a syrup, add water and evaporate again as before, repeating this process until upon renewed addition of a drop of water to the syrup no odor of nitrous acid is perceptible.

Now dissolve in water and filter into a porcelain dish. Add sodium hydrate solution, until strongly alkaline, while the liquid is kept boiling and continue to boil after the addition for a few seconds, during which time a drop or two of alcohol are added. At first the oxides of all the metals are thus formed, but after a while the excess of NaOH transforms Ir, Rh and Pd into the sesquioxides while platinum remains as oxide. Sodium hypochlorite is formed at the same time but this is destroyed by the addition of a little alcohol.

If now HCl be added and the heating continued a yellow precipitate is first formed, while the HCl and the excess of NaOH have just neutralized each other. Heating is continued and more HCl is added until the yellow precipitate is redissolved.

Platinic chloride and the sesquichlorides of Ir, Pd and Rh are formed.

All of these are soluble but only the platinic chloride is precipitated by potassium chloride. To the clear filtrate is added a hot, saturated solution of KCl, until no more precipitate is formed. After cooling, the canary yellow precipitate of  $\text{K}_2\text{PtCl}_6$  is filtered, washed with a solution of KCl saturated in the cold, dried very thoroughly and reduced in a long, absolutely dry Bohemian glass tube by means of hydrogen at a very low temperature. The tube is put in an ordinary combustion furnace and the flames are kept very low.

After all of the double salt has become uniformly black, the mass is allowed to cool in the hydrogen current. The contents of the tube are then transferred to a porcelain dish, boiled with water and decanted, or filtered by decantation. This boiling is repeated until all KCl is dissolved and the wash water does not show the chlorine reaction. The pure platinum obtained is now dissolved in aqua regia, as described above for the impure metal

and the syrup is treated with water until no further escape of nitrous acid takes place.

#### THIRD PORTION.

*Hygroscopic Water.*—Heat the substance (powdered as described), at 105° C. to constant weight. *Water of Combination.*—Heat the material for 15–20 minutes to redness in a Bohemian bulb tube and collect  $\text{H}_2\text{O}$  in a weighed  $\text{CaCl}_2$  tube. Allow to cool in a current of cold, dried air. In case the silicate should contain  $\text{FeO}$ , the heating has to be performed in a current of  $\text{CO}_2$ , since it is desirable to weigh the bulb tube also for control.

#### FOURTH PORTION.

Take a well dried Bohemian glass tube, 1 foot long, closed at one end and put into it, by means of a long weighing tube, about 1 gm. of substance. With the aid of a long capillary funnel tube moisten the mass uniformly with some drops of water. Prepare a mixture of 6 pts. conc.  $\text{H}_2\text{SO}_4$  and 2 pts.  $\text{H}_2\text{O}$ , allow it to cool and pour it through the same funnel tube upon the substance, until it occupies 8 to 10 times the volume of the latter. Reduce the diameter of the tube greatly at about two inches from its open end and replace the air above the liquid with carbon dioxide. Seal before the blast lamp. After cooling shake the tube vigorously in order to avoid caking. Heat the sealed tube for 4 to 5 hours in a thermostat to 200° or 220° C. When quite cold open the tube, transfer its contents, without filtering, into a high beaker, wash rapidly and titrate with permanganate solution, the titre of which has been determined immediately before use. It is evident that in presence of organic matter in the silicate this determination cannot be performed.

#### FIFTH PORTION.

For the determination of phosphoric acid fuse with  $\text{Na}_2\text{CO}_3$  as directed for first portion, but dissolve in  $\text{HNO}_3$  instead of using  $\text{HCl}$ . Reduce the silicic acid to a sandy powder, filter and acidulate with nitric acid. Prepare a solution of ammonium molybdate in

the following manner: 100 grms. molybdic acid suspended in 240 grms. distilled water, of a temperature of about 50° C., are mixed with 160 grms. of  $\text{NH}_4\text{OH}$  of Sp. Gr. 0.91. If necessary, filter and allow *this* solution to run gradually *into* 1250 c. c.  $\text{HNO}_3$  of Sp. Gr. 1.20. Shake at intervals and allow the clear solution to rest for five or six days in a moderately warm, dark place. Decant or syphon, if necessary, from yellow precipitate and add  $\text{H}_2\text{O}$  to make 2 litres. Preserve this reagent in the dark.

In case the amount of phosphoric acid in the sample does not amount to more than one decigramme, and provided the volume of the liquid to be tested does not exceed 150 c. c., add an excess of the above solution of ammonium molybdate and put the beaker into a water bath containing boiling water. Allow the beaker to remain for ten minutes in the boiling water and *all* phosphoric acid will be precipitated.

If the mineral is richer in phosphoric acid it must be treated with an excess of ammonium molybdate in a warm place for fully twenty-four hours.

In either case the precipitate is filtered, washed at first with the molybdate solution used for precipitation, finally with a solution of one-third that strength, obtained by dilution with  $\text{H}_2\text{O}$ . The united filtrates are allowed to stand for a while in order to see if an additional precipitate is formed.

The yellow precipitate on the filter is quantitatively dissolved in  $\text{NH}_4\text{OH}$ .

Magnesium mixture is now prepared in the following manner: Magnesium chloride is dissolved in conc.  $\text{HCl}$  in the proportion of 5 grms.  $\text{MgCl}_2$  to 30 c. c.  $\text{HCl}$ . Dilute with water and supersaturate with strong  $\text{NH}_4\text{OH}$ . If the liquid should not remain clear, but precipitate magnesia, enough  $\text{NH}_4\text{Cl}$  must be added to redissolve this.

Of a solution thus prepared, take a certain volume and divide into halves. One-half is added to the ammoniacal solution of phospho-ammonium molybdate, after this has been nearly neutralized with  $\text{HCl}$ . Finally add strong  $\text{NH}_4\text{OH}$ , amounting to one-third of the entire volume of the liquid. Allow this to stand three to four hours.

Fill up the other half of the magnesium mixture taken, with the same quantity of  $\text{NH}_4\text{OH}$  used in forming the precipitate just described, and then with  $\text{H}_2\text{O}$  to obtain the same volume. A precipitate of magnesia formed here, should be deducted from the previously described one.

The filtration, washing and heating until magnesium pyrophosphate is obtained, takes place according to the description given, I.

#### SIXTH PORTION.

Fluorine is quite frequently found in silicates containing phosphoric acid. To determine F fuse the silicate, duly prepared, with  $\text{Na}_2\text{CO}_3$  as previously described. Boil the cake with  $\text{H}_2\text{O}$  and a little  $\text{NH}_4\text{OH}$  in order to expel  $\text{CO}_2$ , thus preventing solution of either  $\text{SiO}_2$  or alumina. Filter, add  $\text{HCl}$  until the liquid is almost neutral. (Avoid acidity since  $\text{HF}$  might escape.) Digest for some time with  $\text{NH}_4\text{Cl}$  in order to separate all  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , filter if necessary, add  $\text{CaCl}_2$  solution and filter the precipitate consisting of calcium fluoride, calcium phosphate and calcium carbonate. Heat the precipitate to redness in a porcelain crucible. Now, after cooling, add acetic acid and evaporate the mass again to dryness. Continue this treatment with acetic acid, alternating with washing with water and decanting, until the weight of the residue remains constant. In this manner calcium acetate and phosphate are extracted and calcium fluoride remains.

#### SEVENTH PORTION.

In order to determine titanic acid, the mineral is fused with potassium bisulphate, using six to eight times the quantity of this latter. Dissolve the fused mass in a little cold water, dilute strongly and boil slowly in a round flask. From time to time add water, since titanic acid is only precipitated from very dilute solutions. In order to prevent precipitate of Fe add either sulphur dioxide, sodium hyposulphite or  $\text{H}_2\text{S}$  to the liquid, thus reducing  $\text{Fe}_2\text{O}_3$  or avoiding the oxidation of  $\text{FeO}$ . The precipitate of titanic acid is heated and weighed. If not quite colorless repeat the operation.

## EIGHTH PORTION.

For the determination of soluble silicic acid treat the mineral in a platinum crucible with conc. KOH solution upon the water bath for one-quarter to one-half hour. Avoid too great concentration of the liquid, as the silicic acid dissolved would be reprecipitated. If it be suspected that the mineral decomposes, heat only for a short time. The contents of the crucible are transferred to a beaker, diluted strongly, washed by decantation with boiling water until no further reaction of KOH is obtained. The residue is heated and weighed; the operation is repeated until the weight is constant.

If, upon decantation, the precipitate should not settle or should run turbid through the filter, a slight acidulation of the wash water will frequently serve. In case free quartz was present, this would become partly soluble on heating. In such case the mineral is treated several times with KOH solution, decanted each time, as described, but only heated and weighed once, which weight must then suffice.

COLLEGE OF THE CITY OF NEW YORK, May, 1890.

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A CONTRIBUTION TO THE QUESTION OF ASSIMILATION  
OF ATMOSPHERIC NITROGEN.<sup>1</sup>

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By PROF. A. PETERMANN, Ph. D., Gembloux (Belgium).

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Translated by L. H. FRIEDBURG, Ph. D.

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The question of the intervention of atmospheric nitrogen in the nutrition of plants is certainly one of the greatest importance for the chemist as well as for the physiologist.

Almost forty years ago Boussingault and Ville published the

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<sup>1</sup> *Mémoires couronnés et autres Mémoires publiés par l'Académie royale de Belgique*, 1889. Tome XLIV.

*Bulletin de la station agronomique de l'état à Gembloux*, No. 47; Mars, 1890.



results of their researches, which contradicted each other, and since then the question has been under constant discussion.

Chemists, knowing nitrogen as an element very indifferent in respect to combination, have, almost without exception, sided with Boussingault, who maintained that nitrogen did not participate at all in the nutrition of plants, unless it had previously entered the molecule of ammonia or of nitric acid. The question has within a few years assumed a new phase and to-day we must admit that the balance inclines sensibly towards the side of the "Nitrists."

This is not to be understood in the sense of an immediate fixation of elementary nitrogen by the cells (Ville, Franck), but rather of an indirect introduction of it into the nutrition of the plant. In this regard some investigators discuss the question of enrichment of the soil by way of micro-organisms, or consider the fixation of nitrogen by organic matter as going on under the influence of electricity (Berthelot, Dehérain, Gautier and Drouin, Tacke); others defend the opinion that this fixation is provoked by microbes living in a state of symbiosis in the interior of the nodose roots of vegetable plants (Hellriegel and Wilfarth, Bréal).

Considering the naked soil, Schlösing has denied its enrichment by atmospheric nitrogen and he defends his opinion in several papers presented quite recently to the Academy of Paris. The number of soils which he has studied in this regard is daily growing and *he has not yet found a single one which, being void of vegetation, could fix gaseous nitrogen.*

Several authorities, also, (Wolff and Kreuzhage, Atwater, Putensen), have found in the crop of certain vegetable plants *more* nitrogen than was contained in the soil and the fertilizers of artificial cultures, although without always giving an account of other possible sources or losses of nitrogen and without expressing an opinion in regard to the origin of the surplus obtained.

This, it seems to me, in few words, is the actual position of this question.

The purpose of the following research is to contribute to the solution of the "nitrogen problem," establishing from this point of view the complete balance of a culture of lupines, which has

been executed under absolutely determined conditions. I have chosen the lupine, because the "nitrists" consider this vegetable plant as particularly endowed with the faculty of drawing nitrogen from the subtile source of the atmosphere.

In order to state our problem, let us call—

$N^r$  total nitrogen contained in the crop;

$N^s$  total nitrogen contained in the seed;

$N^a$  total nitrogen contained in the soil at the beginning of the experiment;

$N^{a'}$  total nitrogen contained in the soil at the end of the experiment;

$N^e$  total nitrogen furnished by the fertilizer;

$N^p$  total nitrogen contained in the rain water (ammoniacal, nitrous-, nitric-);

$N^{p'}$  total nitrogen contained in the drainage water;

$N^x$  atmospheric nitrogen.

From these figures we are able to deduce the following equation :

$$N^r = N^s + N^a + N^e + N^p + N^x - N^{a'} - N^{p'};$$

from which follows :

$$N^x = N^r + N^{a'} + N^{p'} - N^s - N^a - N^e - N^p.$$

Supposing that each of these items was exactly determined, this second equation will allow us to establish the value of  $N^x$  and to decide whether, in the production of a certain weight of lupines obtained under the conditions of our experiment *there was or was not an intervention of atmospheric nitrogen*. This equation, which must give us a categorical answer for the cultures *without* nitrogenized fertilizer and also for those receiving "nitric" nitrogen may leave us in doubt in regard to those, the fertilizers of which contain ammoniacal or organic-nitrogen. For, we know, according to the researches of Reiset, Ville, Lawes and Gilbert, König, Morgen, Schlösing and Pichard, that nitrification causes a loss of free nitrogen, which is insignificant or *nil* in the case of slow nitrification of organic nitrogen of the soil; it is a little higher at that of ammonia but important enough in case of nitrification of organic nitrogen of fertilizers. If the arrangement of our ex-

periments allows us with certainty to trace the nitric nitrogen which results from this oxidation and to find it again in the plant, or the soil or waters of drainage, this is altogether different for the emanation of elementary nitrogen, the determination of which escapes us. A gain in nitrogen noted in this case is therefore necessarily a minimum, if this gain be not hidden through a loss of elementary nitrogen.

For this first series of experiments I have put aside the question as to how, by what mechanism or chemism, the intervention of elementary nitrogen might eventually take place. I desired above all to settle the question *whether* the fixation of gaseous nitrogen takes place, because, as I have said before, the question is far from being decided.

The arrangement of our experiments should also permit us to verify the assertion of certain nitrists, who, in spite of the culture experiments of Proost<sup>1</sup> and others, pretend that the faculty of certain leguminous plants to transform elementary nitrogen into organic substance, exists to such a high degree, that they will not utilize, or only utilize in an absolutely insignificant proportion, the nitrogen offered to them in the form of fertilizing matter.

Our experiments have been performed in vegetation compartments the perfect description of which we have given in our paper, a contribution to the chemistry and physiology of the sugar beet.<sup>2</sup> We refer here to the fact that the arrangement of these boxes allows to realize the following advantages:

1. A perfect separation of the experimental soil, as well as the fertilizing elements and the liquids circulating in that soil, from the surrounding earth.

2. Equal exposure of all boxes to rain, heat and light.

3. The compartments receive exclusively that quantity of rain which falls on the surface of one square metre, and all danger of loss of water is avoided. From this it is evident that all the vegetation boxes are under conditions absolutely comparable.

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<sup>1</sup> Revue des questions scientifiques, 1886.

<sup>2</sup> Mémoires couronnés et autres mémoires publiés par l'académie royale de Belgique, 1889; vol. XLIII.

With respect to the special point of this study of the nitrogen question, I add, that the dimensions of the vegetation boxes offer this great advantage: they admit of experimentation in each case with a certain number of plants (36) and thus of work independent of the influence of the individuality of the plants themselves. I am convinced that one of the principal causes which has led to contradictory conclusions, so frequent in physiological research, is to be found in the non-observance of this rule of experimentation.

#### CONCLUSIONS.\*

1. In growing plants of yellow lupines (*Lupinus luteus*) in sand containing the bacteria of soil, but very poor in nutritive elements, using vegetation compartments so arranged as to allow a perfect control of all conditions of the experiment and further, accurately determining the proportion of nitrogen contained in such sand before and after the experiment, as well as in the seed, the waters of rain and drainage, and in the crop, we observe finally, considering the total of roots, soil and aerial part, an important gain in nitrogen, due to the intervention of atmospheric nitrogen.

2. This gain increases with the quantity of organic substance produced. In our experiments it amounted to three times the quantity of the mineral fertilizer (potassium and magnesium sulphates) used. This phenomenon does exist, when an abundance of sodium nitrate is used as a fertilizer. The gain is partly hidden by a loss of elementary nitrogen, due to the nitrification of ammonia and of organic nitrogen in the compartment, where the sodium nitrate was replaced by an equivalent quantity of nitrogen in the form of ammonium sulphate or of dried blood (sterilized).

3. Contrary to the opinion of some authors, our experiments proved, that the lupines absorbed and assimilated (that is

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\*Concerning the raw material used as well as the mode of procedure followed and the detailed analytical data, we refer to: *Bulletin de la station agronomique de l'état a Gembloux*, 1890, No. 47. From these extensive experiments, the following conclusions were reached. L. H. F.

to say utilized for the production of organic substance) nitrogen which was furnished in the form of a fertilizer.

4. The nodes of the roots of lupines are sensibly richer in nitrogen than the rest of the plant, particularly in those experiments which show an increase of nitrogen. However, this observation cannot be used as a support for the hypothesis according to which the presence of nodosities, or of microbes inhabiting the same, should be the exclusive cause of the assimilation of atmospheric nitrogen :

(a.) Because the increase of nitrogen is not only noticeable in the plant alone, but also in the soil ;

(b.) Because the gain of nitrogen by enrichment of the soil has been obtained in the culture of plants which did not possess nodosities upon the roots.

5. The pure culture proves the identity of micro-organisms of the soil in which the lupines grew with those occurring in the nodosities of the root of this plant.

I stated at the beginning of this paper, that the aim of my study was to contribute to the nitrogen question, by taking account of nitrogen furnished and lost in a culture of lupines, performed under conditions which would give complete control of the course of the experiment, in order to decide whether an intervention of atmospheric nitrogen exists or not. I have to conclude by answering this question in the affirmative.

This first statement being now made, we shall have to ask in addition whether the important increase which balances our account of lupine culture can be explained (in spite of the small probability which a calculation, based upon the researches of Schloësing offers) by the presence of *combined* nitrogen, diffused through the atmosphere, or whether it must really be attributed to an intervention of *elementary* nitrogen.

A new series of experiments, performed under particular conditions, will allow us to answer this part of the question. We shall also repeat the above experiments with other leguminous plants and finally with other families of plants.

## ABSTRACTS.

### GENERAL AND INORGANIC CHEMISTRY.

#### Determination of the Atomic Weight of Bismuth. ALEX. CLASSEN.

Three methods of preparing pure bismuth were followed. 1. Bismuth, called *purissimum* in commerce, was used. Of this 250 grms. were dissolved in nitric acid, evaporated and the residue repeatedly evaporated with HCl, until all  $\text{HNO}_3$  was driven off. The bismuth chloride, dissolved in conc. HCl was stirred with alcohol and the lead chloride filtered off. The solution was then divided into ten beakers of four liters capacity each and by addition of water, oxychloride was precipitated. The precipitates were washed by decantation, until no more HCl was present, then redissolved in conc. HCl and again precipitated by water. This operation was repeated twelve times. At last the bismuth oxychloride was taken up with conc. HCl, diluted a little with water and precipitated by  $\text{NH}_4\text{OH}$  and ammonium carbonate. Washing by decantation followed, until no more ammonia was present. Again the precipitate was dissolved in conc. HCl and reprecipitated with ammonia and ammonium carbonate. This process was repeated three times. Finally the different precipitates were dissolved in conc. HCl and again  $\text{BiOCl}$  was precipitated. This was washed, dried and fused with 98 per cent. KCN in a porcelain crucible. The reduced metal again was fused several times with KCN. The regulus was freed from KCN, but not before the mass was absolutely cold. The metallic globules were washed with water and polished on the turn-table. When thus put into closed flasks the metal retains its bright surface for months.

2. The method was practically the same as above, only the raw material was "*bismuth subnitras purissimum*" of commerce, from the same source from which Marignac bought his in times past. The spectrum analysis showed, however, that in spite of all care, lead was retained in the metal. When the nitrate solutions of the

metal obtained were treated electrolytically, lead was found in every one.

3. The bismuth was obtained by electrolysis, with peculiar precautions, from the metal prepared as above dissolved in pure  $\text{H NO}_3$ . About 3 kilos. of the absolutely pure metal were thus obtained. The atomic weight was calculated from bismuth oxide, which, after critical consideration, was considered the safest way. According to this research the atomic weight of bismuth is :

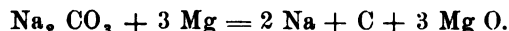
For O = 16 .....	208.89830.
“ “ = 15,96 .....	208.37605.

(*Ber. d. Chem. Ges.*, **23**, 938, 1890.)

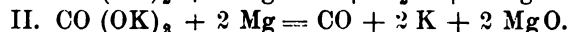
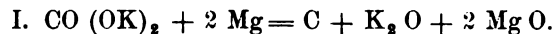
L. H. F.

#### Reduction of Oxygen Compounds by Magnesium. CLEMENS WINKLER.

I. The compounds of elements which, according to the periodic law form the first group, were subjected to this action. Carbonates, hydrates or oxides (according to the ease with which they can be prepared in a pure state) and powdered magnesium were used. The following metals were thus obtained: Na, Li, K, Rb and Cu. Rubidium was reduced with especial facility, so that its preparation in a metallic state from the carbonate in this way is recommended; Cs, Ag and Au were not reduced by Mg. Some of the reductions can be expressed in reactions:



In regard to potassium, the author thinks it likely that it may advantageously be *manufactured* in this way. Further it was found that two of the oxygen atoms in potassium carbonate are more easily taken up by Mg than the third one, showing that the OK group is more easily reduced than CO, and thus proving the correctness of the constitutional formula:  $\text{CO (OK)}_2$ . The experiment proved that the *second* of the following two equations had been realized :



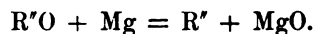
Also the hydrate was easily reduced :



Gold suboxide was reduced by heat alone and was found along with the unchanged magnesium. (*Ber. d. Chem. Ges.*, 23, 44, 1890.)  
L. H. F.

II. This research comprises the second group, viz.: Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg.

The quantitative proportion in which the oxides of these elements were subjected to the treatment with Mg at high temperatures is indicated in the following:



In some cases also the hydroxides were used.

Beryllium was reduced. Magnesium acting upon magnesium oxide did not produce a suboxide. The reaction performed in a current of hydrogen yielded magnesium crystals of definite shape, seemingly hexagonal; magnesium oxide remained unchanged. Calcium was reduced from its oxide (obtained from marble) but could not be obtained as a regulus. When calcium hydrate was used, calcium as well as hydrogen resulted. It was also shown that magnesium reduced water at high temperatures. Strontium oxide was reduced to strontium, an almost homogenous cylinder consisting of magnesium oxide and metallic strontium was obtained, which retained its consistency when used for a flame reaction in a Bunsen burner. When this mass was heated on a red hot cover of a porcelain crucible the beauty of the flame was dazzling. Barium oxide yielded results similar to those of Ca and Sr; the metal could not be obtained as a regulus. Zinc was reduced but not obtained, being lost by evaporation, as also was mercury. Cadmium coated the whole inside of the operating tube. (*Ber. d. Chem. Ges.*, 23, 120, 1890.)

III. The third group, containing B, Al, Sc, Y, La, Yb, Ga, In, Tl, were now, as far as available, taken up for this study. Boracic anhydride and borates, under this action, furnished magnesium boride and a liquid as well as a gaseous compound of boron with hydrogen. The body  $BH_3$  was not formed. Aluminium oxide did not furnish pure aluminium. A monoxide,  $AlO$ , was formed besides magnesium spinell:  $MgAl_2O_4$ . The monoxide was not prepared in a pure state. Yttrium was reduced from its oxide;



lanthanum mixed with magnesium oxide was obtained from its carbonate. The amount of gallium oxide used (0.1 grm.) was too small to show a satisfactory result. No regulus of indium could be detected with a lens, when indium oxide was used. Thallium oxide showed reduction in part, but the suboxide was principally formed while thalious carbonate was reduced. (*Ber. d. Chem. Ges.*, **23**, 772, 1890.) L. H. F.

**Preparation of a very Active Platinum Black.** O. LOEW.

Fifty grms. of platinic chloride dissolved in 50–60 c. c. in water are mixed with 70 c.c. of formaldehyde of 40–45%. Keeping the mixture cool and adding a solution of 50 grms. Na OH in 50 c.c.  $H_2O$ , the greater quantity of the metal is at once separated. After twelve hours, filter with the pump. A yellow liquid runs off, which, on boiling, deposits a little platinum. After the salts are washed out (which is very essential for a good, active platinum black), a deep black solution filters through, some of the exceedingly fine sponge being dissolved. The last traces of salts are separated easily by dialysis, and a deep black translucent liquid results. This, when shaken with a little air and alcohol, instantly develops aldehyde; it also decomposes hydrogen peroxide energetically and thus seems to be a watery solution of platinum, analogous to Muthmann's red solution of elementary silver. The black sponge on the filter begins to absorb oxygen, the temperature rises to 36°–40° C. and bubbles of gas burst forth accompanied by a hissing sound. Then the fine pulp is spontaneously transformed into a porous mass, which is finally washed and dried over sulphuric acid. (*Ber. d. Chem. Ges.*, **23**, 289, 1890.) L. H. F.

**On Beryllium.** GERHARD KRÜSS and HERMANN MORAHT.

A kilo. of light green colored leucophane from Arendal in Norway was the starting point of this research. The metal was reduced from its hydrate by magnesium, but could not be obtained pure enough in this way. Then the compound  $K_2 Be F_4$  was prepared and the metal was successfully reduced in the form of hexagonal crystals by means of sodium. (*Ber. d. Chem. Ges.*, **23**, 727, 1890.)

L. H. F.

**An Apparatus for Preparing Chlorine.** PETER KLASON.

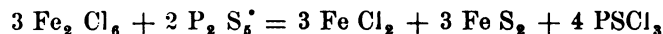
This apparatus is made of clay and resembles in action that of Kipp. Warm water is used as a source of heat. The rubber stoppers, when covered with vaseline, resist the action of chlorine gas perfectly. (*Ber. d. Chem. Ges.*, **23**, 330, 1890.) L. H. F.

**Chemical Analysis of a Meteorite of Carcote.** (Chile.) W. WILL and I. PINNOW.

Besides iron chromate, the presence of two different silicates were analytically indicated. One, containing the elements according to the formula of olivine,  $(\text{Mg Fe})_2 \text{SiO}_4$ , the other, of the composition  $\text{R}'' \text{SiO}_3$ , in which 3  $\text{R}'' \text{O}$  are partly replaced by  $\text{Al}_2 \text{O}_3$ . (*Ber. d. Chem. Ges.*, **23**, 345, 1890.) L. H. F.

**Synthesis of Iron Pyrites.** E. GLATZEL.

Differs from the methods of Berzelius, Wöhler and others, in that the formation of  $\text{FeS}_2$  is attained according to the equation:



The iron disulphide thus prepared is obtained quickly and easily in microscopic crystals of very perfect form and of a bright brassy lustre. (*Ber. d. Chem. Ges.*, **23**, 37, 1890.) L. H. F.

**Stereochemical Considerations.** ALEX. NAUMANN.

The greatest possible effect of the attractive force between carbon atoms takes place when the directions of attraction coincide with the line which unites the centres of gravity of two such atoms. If the directions of attraction deviate from this line, only that component of the total attraction links the atoms which lies in the direction of this line. (*Ber. d. Chem. Ges.*, **23**, 477, 1890.) L. H. F.

**ORGANIC CHEMISTRY.****A New Hexylamine and a New Hexyl Alcohol.** MARTIN FREUND and PAUL HERRMANN.

A vacancy exists in the hexyl series. Eight acids are theoretically possible, seven of which have been found; only four primary

alcohols and but two corresponding amines are known. Some derivatives of diethylacetic acid were prepared. The  $\Psi$ -hexylalcohol ( $C_6H_{13}$ ),  $CH_3CH_2OH$ , which may be called diethylcarbin carbinol, possesses an odor suggestive of camphor and at the same time of fusel oil; it boils between  $139^\circ$ – $143^\circ$  C. This is a comparatively low boiling point. But in comparison with the corresponding acids an approximately equal difference is observed :

Normal caproic acid	boils at	$205^\circ$ C.		
Normal hexyl alcohol	" "	$157.2^\circ$ ;	diff :	$47.8^\circ$
Isobutylacetic acid	" "	$199.7^\circ$		
Isohexyl alcohol	" "	$150^\circ$	"	$49.7^\circ$
Methylisopropylacetic acid	" "	?		
Pentyl carbinol	" "	$152.5^\circ$	"	?
Methylpropylacetic acid	" "	$195.4^\circ$		
Methylpropylcarbin carbinol	" "	$146.8^\circ$	"	$48.6^\circ$

To these must now be added :

Diethylacetic acid, boiling at	$190^\circ$ C.		
Pseudo-hexyl alcohol " "	$141^\circ$ C.	"	$49^\circ$
(Ber. d. Chem. Ges., 23, 189, 1890.)		L. H. F.	

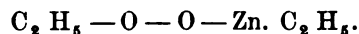
#### A Compound of Calcium Chloride and Normal Propylic Alcohol, which Moves on Water. CHRISTIAN GÜTTIG.

A solution of anhydrous calcium chloride in normal propylic alcohol yields crystals of the composition  $CaCl_2 + 3C_3H_7O$ , which, like the compounds of alkalies and alcohols, moves actively upon water until dissolved, without evolution of a gas. (Ber. d. Chem. Ges., 23, 181, 1890.) L. H. F.

#### Action of Oxygen upon Zincethyl. ROBERT DEMUTH and VICTOR MEYER.

Frankland stated that he obtained  $Zn(OC_2H_5)_2$  when oxygen acted upon a dilute solution of zincethyl. According to this, the two oxygen atoms would have been interpolated between zinc and carbon. The body on which Frankland reported and which he called zincethylate, is highly explosive when heated, particularly at reduced pressure. The authors attempt to prove that the sub-

stance in question is not zincethylate, but a compound of the structure of peroxides, particularly as it decomposes potassium iodide with liberation of iodine. On distillation with dilute  $\text{H}_2\text{SO}_4$  alcohol is formed. It is, therefore, more probable that this body has the formula :



(*Ber. d. Chem. Ges.*, **23**, 394, 1890.)

L. H. F.

### Formation of Anhydrides in the Succinic Acid Series.

VICTOR MEYER and KARL AUWERS.

This formation is facilitated in a remarkable degree by introduction of methyl groups into the molecule. The tetramethylated succinic acid is entirely transformed into its anhydride (which greatly resembles camphor) on mere distillation, or on heating with aqueous  $\text{HCl}$  in a pressure tube. A comparative research of all methylated succinic acids in regard to the relative ease with which they split off water is recommended. (*Ber. d. Chem. Ges.*, **23**, 101, 1890.)

L. H. F.

### Tetramethylsuccinic and Trimethylglutaric Acid.

KARL AUWERS and VICTOR MEYER.

This research proved the difference in structure of the two isomeric acids by a new method, revealing the structure of fatty acids by their behavior towards bromine. (*Ber. d. Chem. Ges.*, **23**, 293, 1890.)

L. H. F.

### Facts About Paraffin. B. PAWLEWSKI.

Paraffin, when treated with solvents, behaves like a colloid. It yields jellies with benzol, chloroform and especially with ether. In acetic acid it behaves like a crystalloid. The presence of paraffin in crude petroleum, in the form of vaseline, may thus be explained. (*Ber. d. Chem. Ges.*, **23**, 327, 1890.)

L. H. F.

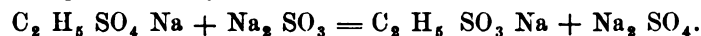
### Synthesis of Glucose. EMIL FISCHER.

Gluconic acid when treated with sodium amalgam in a cold acid solution is transformed into grape sugar. The dextro-mannose (the synthesis of which is described p. 165) is stereo-isomeric with glucose. We have seen that dextro-mannose was prepared, after a

number of transformations, from formaldehyde. Dextro-mannose yields an osazone, the mannosephenylhydrazone. A mannonic acid lactone was prepared, and from this mannonic acid. Now mannonic acid has been transformed into the above mentioned gluconic acid, which yields glucose. These results are now available for theoretical considerations in regard to the process of assimilation by plants. (*Ber. d. Chem. Ges.*, **23**, 799, 1890.) L. H. F.

**A New Preparation of Ethylsulphonic Acid.** FRIEDRICH MAYER.

Sodium ethylsulphate is treated with sodium sulphite in closed tubes or pressure bottles at 110°–120° C. The reaction runs almost quantitatively, thus :



(*Ber. d. Chem. Ges.*, **23**, 908, 1890.)

L. H. F.

**On Propylamine.** S. GABRIEL and W. E. LAUER.

It was found that the halogen is also easily replaceable in the propyl compounds and thus permits of many peculiar reactions. The compound of  $\beta$ -brompropylamine with HBr reacts with potassium cyanate to form trimethylene- $\Psi$ -urea. (*Ber. d. Chem. Ges.*, **23**, 87, 1890.)

L. H. F.

**Anhydro-bases from Amidomercaptans of the Fatty Series.** S. GABRIEL and PH. HEYMANN.

Thiobenzamide and ethylenebromide were allowed to react together and thus  $\mu$ -phenylthiazoline,  $\text{C}_6\text{H}_5\text{NS}$  was formed. When a hydrochloric acid solution of this basis was oxidized with bromine water, benzoic acid and taurin,  $\text{SO}_3\text{H.C}_6\text{H}_4\text{NH}_2$ , separated from a syrup, which was the direct result of that oxidation, and which, doubtless, contained benzoyltaurine. The formation of this latter from phenylthiazoline is easily explained. (*Ber. d. Chem. Ges.*, **23**, 157, 1890.)

L. H. F.

**Xylose and Wood Gum from Straw and other Material.** E. W. ALLEN and B. TOLLENS.

Cherry wood, straw or loofah are extracted with caustic soda. The extract is precipitated by means of alcohol, thus yielding gum,

of which straw from wheat furnished 16 per cent., and this, subjected to hydrolysis, furnished xylose. (*Ber. d. Chem. Ges.*, **23**, 187, 1890.) L. H. F.

**Action of Chlorine on Phloroglucine.** TH. ZINCKE and O. KEGEL.

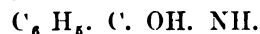
As previously shown, chlorine acts upon phloroglucine, in chloroform solution, to produce hexachlortriketone:  $C_6Cl_6O_3$ . Stannous chloride reduces this to trichlorphloroglucine. The hexylene ring existing in hexachlortriketone is very easily broken, even by water, which splits it into  $CO_2$ ;  $CHCl_2COOH$  and  $CHCl_2CO.CHCl_2$ . A hexachloracetylacetone could not be obtained, but octochlor or hexachlordibrom derivatives were prepared. Treated with ammonia, the hexachlortriketone furnishes dichloracetamide only. When  $PCl_5$  is allowed to react with hexachlortriketone, hexachlorbenzol,  $C_6Cl_6$ , is formed but no  $C_6Cl_{12}$ . (*Ber. d. Chem. Ges.*, **23**, 230, 1890.) L. H. F.

**Alkylation of Acid Amides.** JULIUS TAFEL and CARL ENOCH.

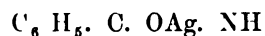
Benzamide and anisamide were used. It is well known that, although hydrogen in acid amides may partially be replaced by metals, such as silver or mercury, these amides will *not* yield alkylamides under the influence of alkyl iodides.

Now it was found, that, under certain conditions, benzamide may be ethylated, but that the product of reaction is not ethylbenzamide but benzimidoethyl ether, which formerly had been obtained from benzonitrile with alcoholic  $HCl$ .

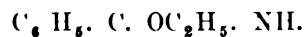
So far only aromatic amides have permitted a successful reaction of this kind. It is surmised, therefore, that the real constitution of these amides, taking benzamide as an example, is



The corresponding silver salt :



and the ethyl ether :



This reaction takes place between ethyl iodide and silver benz-

amide at ordinary temperature. (*Ber. d. Chem. Ges.*, **23**, 103, 1890.)  
L. H. F.

**Synthesis of Alcohols in the Pyridine Series.** ALFRED EINHORN.

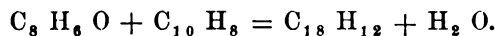
Since cocaine has been recognized as a derivative of pyridyl- $\beta$ -lactic acid, the author has successfully endeavored to prepare this latter from  $\omega$ -trichlor- $\alpha$ -oxypropylpyridine:  $C_5H_4N.CH_2CHOH.CCl_3$ , which had been formerly described as prepared (as a condensation product) from  $\alpha$ -picoline with chloral. The work will be continued and the products of reduction will be taken up as the next step. (*Ber. d. Chem. Ges.*, **23**, 219, 1890.)  
L. H. F.

**Symmetrical Tetrabromdiacetyl.** H. F. KELLER.

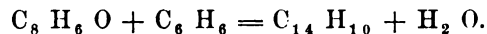
This compound was prepared directly from diacetyl; the reaction does *not* stop at the dibrom derivative but proceeds slowly towards the tetra product, which is thus obtained almost quantitatively. The properties proved to be the same as those of the tetrachlor-diacetyl prepared by Levy, Jedlichka and Witte from chloranilic acid by means of  $KClO_3$  and  $HCl$ . This fact removes the last doubt as to the constitution of tetrachlor-diacetyl and shows its connection with diacetyl. (*Ber. d. Chem. Ges.*, **23**, 35, 1890.)  
L. H. F.

**Synthesis of Chrysene and Related Hydrocarbons.** G. KRAEMER and A. SPILKER.

The vapors of naphthalene and cumarone, when jointly passed through an iron tube kept at dull red heat, are decomposed with surprising facility, forming water and chrysene:



Cumarone and benzol distilled together through the same apparatus furnished phenanthrene:



(*Ber. d. Chem. Ges.*, **23**, 84, 1890.)  
L. H. F.

**Isocinnamic Acid Present in the Alkaloids accompanying Cocaine.** C. LIEBERMANN.

The alkaloidal by-products of cocaine are now technically worked for ecgonin, and thus the raw material for the study of acids split off from these, is more abundantly obtainable. Isocinnamic acid was recognized in them and has subsequently also been found in storax. (*Ber. d. Chem. Ges.*, **23**, 141, 1890.)

L. H. F.

**Action of Carbon Disulphide upon Menthol and Borneol.** EUG. BAMBERGER and W. LODTER.

Menthylxanthogenic acid:  $C_{10}H_{11}O$ . CSSH and bornylxanthogenic acid:  $C_{10}H_{11}O$ . CSSH were prepared, showing the similarity of these camphor alcohols with alicyclic  $\beta$ -tetrahydronaphthol, discussed by the authors in a paper of great length immediately preceding. (*Ber. d. Chem. Ges.*, **23**, 213, 1890.)

L. H. F.

**Note on Camphoric Acid.** EUG. BAMBERGER.

Experiments showed that at 100° to 120° C. no HBr addition-product could be obtained, nor was the acid attacked by potassium permanganate. Victor Meyer had previously proved that this acid was indifferent to nascent hydrogen. The author concludes therefore that there exists *no* double linking in the molecule of camphoric acid, but that this acid is a tetramethylene derivative. (*Ber. d. Chem. Ges.*, **23**, 218, 1890.)

L. H. F.

**Adenine and Hypoxanthine.** G. BRUHNS.

Want of clearness and many errors in regard to the properties of hypoxanthine and of the occurrence of adenine are ascribed to the fact that there exists an adenine-hypoxanthine which the author has prepared. This compound has the formula  $C_6H_4N_4O$ .  $C_6H_5N_5 + 3H_2O$ . It forms an homogeneous hydrochloride, differing in form from either adenine hydrochloride or hypoxanthine hydrochloride. (*Ber. d. Chem. Ges.*, **23**, 225, 1890.)

L. H. F.



**Triphendioxazine by Oxidation of Orthoamidophenol.**

PAUL SEIDEL.

The oxidation was performed by heating orthoamidophenol hydrochloride with 30-40 times its weight of water in a flask, attached to a reflux condenser on the water bath, passing at the same time a vigorous current of air through the solution. The raw product obtained was purified successfully only by sublimation. This latter took place upon cast iron plates of 25 cm. diameter, having an upturned edge  $\frac{1}{2}$  to 1 cm. broad and 2 to 3 cm. high. Glass plates or unglazed clay plates were used as covers, while a layer of asbestos served as a packing. Three grms., on an average, of perfectly pure crystals could be obtained on one plate. The raw product yields 40 to 60 per cent. substance sufficiently pure for analysis. The substance is a red dye. In all conc. acids it is soluble with deep blue coloration, forming salts, which are decomposed by water. Leuco compounds were prepared and the constitution of the dye was also ascertained by the following synthesis. One mol. of symmetrical diamidoresorcin sulphate heated with two mols. sublimed amidophenol yields a green vapor, which condenses to beautiful red crystals. These latter are identical with the product obtained as described above. Consequently, the dye contains the chromophore group  $N_2$  and must be named triphendioxazine. (*Ber. d. Chem. Ges.*, **23**, 182, 1890.)

L. H. F.

**The Cumarone of Coal Tar.** G. KRAEMER and A. SPILKER.

In the neutral distillates of hydrocarbons from coal tar, remarkable quantities of a substance were found, along with small amounts of a substance containing nitrogen. This latter is nothing but benzonitrile, to which is due, without doubt, the presence of benzoic acid in tar oil or in the residues from phenol. The first mentioned substance is the cumarone, the presence of which in coal tar has so far been unknown. The cumarone is obtained from the well fractioned parts of light tar oils, boiling between 168° and 175° C., after these have been treated successively with caustic alkalies and mineral acids, in order to free them from their constantly associated phenols and pyridine bases. To a kilo. of

strongly cooled tar oil, thus prepared, 450 grms. of bromine were slowly added and the dibromocumarone,  $C_8H_6Br_2O$ , was obtained in the shape of large, prismatic crystals, soluble in chloroform and by means of this rendered quite pure, showing the melting point  $88^{\circ}$ – $89^{\circ}$  C. As several kilos. of cumarone were at the disposal of the authors, the older data were re-examined and corrected. Cumarone boils at  $170^{\circ}$ – $171^{\circ}$  C. It represents a very permanent and constant compound; thus it distills off almost without loss from charring when slowly dropped upon melting KOH. Boiling KOH solutions, alcoholic or aqueous, do not attack it. Chlorine substitution products were obtained. With iodine it does not combine at ordinary temperatures. When heated together with iodine, a violent reaction takes place, and the entire mass becomes resinous. Strong mineral acids, *e. g.*, conc.  $H_2SO_4$ , transform the cumarone into a resin, representing a polymeric cumarone, called paracumarone. (*Ber. d. Chem. Ges.*, **23**, 78, 1890.)

L. H. F.

**Synthesis of Indigo from Monobromacetanilide.** W. FLIMM.

This is the first synthesis of indigo from a mono substitution product of benzol. Caustic alkalies acting upon monobromacetanilide (m. p.  $131$ ,  $5^{\circ}$  C $^{\circ}$ ) give rise to different products according to the conditions of work. Aqueous potassium or sodium hydrate destroys the molecule, with formation of aniline and isocyanphenyl. Alcoholic potash acting upon monobromacetanilide gives rise to diphenyldiketonpiperazin. The author added to a solution of monobromacetanilide in absolute alcohol the calculated quantity of sodium, also dissolved in absolute alcohol, and allowed the mixture to stand for a day at the ordinary temperature of the room. Thus ethoxylacetanilide was formed as a faintly yellow oil. But, if monobromacetanilide is melted together with dry caustic alkali, a fused mass is obtained, the solution of which in water soon turns blue and separates indigo; aniline and isocyanphenyl are also formed. The yield is small, not more than 4 per cent. of the anilide used. The author explains the reaction thus: indigo is not directly formed, but at first either indoxyl or pseudoindoxyl,

then by oxidation this intermediate product (which could not be obtained) is changed into indigo. (*Ber. d. Chem. Ges.*, **23**, 57, 1890.)  
L. H. F.

**Decomposition of Alicyclic (1:5-Tetrahydronaphthylenediamine) into its optically active components.** EUG. BAMBERGER.

Amongst the hydrized naphthalene bases there exist two which contain asymmetric carbon atoms, the alicyclic  $\alpha$ -tetrahydronaphthylamine and the alicyclic 1,5-tetrahydronaphthylenediamine. Both are optically inactive, because they represent (according to their synthesis) compounds of enantiomorphous part-molecules. The diamine was used and Pasteur's method was applied for the splitting of this base into its components, acting as optically equal but in an opposite sense. Salts of dextro- and laevo-tartaric acid, with optically active bodies, show different solubility. Hydrized naphthylenediamine was added to a solution of dextro-tartaric acid in the proportion to form the bitartrate; the base dissolved at once, but the concentrated syrup would not crystallize. Then a minute fragment of a crystal of coniin dextro-tartrate was dropped into the liquid, which soon caused the entire syrup to become a crystalline magma. The bitartrate was filtered, decomposed, pressed and treated with HCl gas in ethereal solution; the hydrochloride was obtained and crystallized from water in thick prisms. This salt turned the plane of polarization to the left. The syrup, filtered off from the bitartrate crystals, yielded, after several months' standing, the enantiomorphous form of alicyclic hydronaphthylenediamine. It was also transformed, as above, into the hydrochloride, which crystallizes beautifully and turns the plane of polarization to the right. The corresponding values of rotation are approximately equal. (*Ber. d. Chem. Ges.*, **23**, 291, 1890.)  
L. H. F.

**On Dextro-Cocaine.** ALFRED EINHORN and ALBERT MARQUARDT.

Dextro-ecgoninmethylester and benzoylchloride when heated together to 150°-160° C. furnish, dextro-cocaine quantitatively.

This substance behaves physiologically like common cocaine but with the difference that the local anæsthetic action begins sooner and disappears in shorter time. (*Ber. d. Chem. Ges.*, **23**, 468, 1890.)  
L. H. F.

**Coloring Matter in Yolk of Eggs.** S. BEIN.

The yellow coloring matters from yolk of different kinds of eggs have been called luteines. They may be extracted by ether, alcohol and chloroform. Nitric acid turns them first blue, then yellow. They show 2-3 characteristic bands in a spectroscope. The author claims that air acts upon these coloring substances, particularly when exposed to light. Thudicum's color reactions do not prove, therefore, the absence of yolk of egg in mixtures, nor do they always signify its presence, especially not when nitrogenized products of decomposition are present in these mixtures. (*Ber. d. Chem. Ges.*, **23**, 421, 1890.)  
L. H. F.

**Synthesis of Mannose and Laevulose.** EMIL FISCHER.

The author has now achieved the synthesis of mannit and of laevulose, starting from acroleinebromide, or glycerose or from formaldehyde. All intermediate products were obtained and thus the synthesis of all bodies belonging to the mannit series, except glucose and its derivatives, has been realized. (*Ber. d. Chem. Ges.*, **23**, 370, 1890.)  
L. H. F.

**Hydrazine from Aldehyde Ammonia.** TH. CURTIUS and R. JAY.

Sodium nitrite acting upon a faintly acidulated solution of aldehyde ammonia yields a nitrosamine, the paraldimine  $C_6H_{11}O_2$ . C. (N H). H, a liquid, volatile base, which forms paraldehyde and ammonia gas when treated with water. A nitrosoparaldehyde was prepared, which is identical with the product obtained directly from aldehyde ammonia by means of nitrous acid. This is a lemon-yellow liquid of camphor-like odor. Moist HCl acting upon nitrosoparaldehyde in ethereal solution gives rise to paraldehyde hydrochloride; if a second molecule of water reacts with this latter, paraldehyde and ammonium chloride are formed.

The two latter reactions result jointly when the nitroso compound is boiled with acids. The reduction of nitrosoparaldehyde by means of zinc dust and glacial acetic acid in ethereal solution led to amidoparaldehyde. The hydrochloride of this base, when boiled with dilute sulphuric acid, takes up water and furnishes hydrazin and paraldehyde:  $C_6H_{11}O_2.HC:N.(NH_2) + H_2O = C_6H_{11}O_2.CO.H + N_2H_4$ . The yield of hydrazin is not satisfactory. (*Ber. d. Chem. Ges.*, **23**, 740, 1890.) L. H. F.

**On E. Guinochet's Isomeric Carballylic Acid.** ROBERT DEMUTH and VICTOR MEYER.

This acid was found to be succinic acid. Guinochet worked correctly, but has made a mistake in his interpretation. (*Ber. d. Chem. Ges.*, **23**, 529, 1890.) L. H. F.

**Stereochemical Arrangement of Atoms in Molecules containing Nitrogen.** A. HANTZSCH and ALFRED WERNER.

The main cause for the hypothesis developed here is to be found in the fact, that the attempt to explain the isomeric monoximes and dioximes of benzil in a stereochemical manner led to a conflict with the second proposition of van't Hoff.

The authors overcome this difficulty by assuming that the three valencies of the trivalent nitrogen atom (and perhaps also those of other polyvalent atoms) do not, under all conditions, lie in the same plane with the nitrogen atom.

In hydrocyanic acid, for example, the stereochemical view in regard to carbon could not be entertained, if it were not at the same time admitted that the directions of the valencies of nitrogen deviate from their original direction, and that consequently these latter cannot lie in one and the same plane. Maintaining that the three nitrogen valencies (as we find them in  $NH_3$  and similar compounds) do lie in a plane, the authors surmise that in certain compounds containing nitrogen, its three valencies are directed towards the three solid angles of an irregular tetrahedron, while the nitrogen atom occupies the fourth one. Consequently the angles which these directions form with one another are *not* coincident with those of the valencies of a carbon atom. (*Ber. d. Chem. Ges.*, **23**, 11, 1890.) L. H. F.

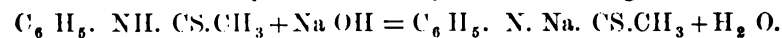
**Substitution Dependent of the Atomic and Molecular Magnitude of the Substituting Bodies.** FRIEDRICH KEHRMANN.

Facts observed in the study of quinon-oximes seem particularly to indicate that the ease of substitution is approximately proportional to the molecular magnitude of substituting bodies already present. This should be understood to mean that any substitution results all the more easily as the molecule of that substituting element, which, by reason of its position, governs the place of substitution, is smaller. (*Ber. d. Chem. Ges.*, **23**, 130, 1890.)  
L. H. F.

**Determination of the Constitution of Tautomeric Compounds.** H. GOLDSCHMIDT and A. MEISSLER.

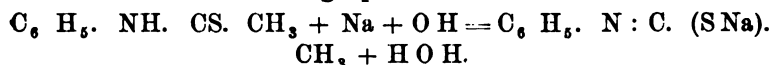
According to Laar, those compounds are called *tautomeric* which apparently react in a manner indicated by two constitutional formulæ differing from each other. Laar assumes that in such bodies the atoms oscillate between two different positions of equilibrium. This interpretation does not at all permit the use of the words "constitutional formulæ," in the proper sense of the word, which would only permit *one* of those positions (recognized from allied reactions) to be considered as correct. The other position would not belong to the substance *per se*, because the reactions according to which it has been derived, have caused a change of position of atoms within the molecule. Incorrect formulation of the chemical equations for these reactions may be the reason for the apparent contradiction of the principles of structural chemistry which these phenomena of change within the molecule offer.

According to Ostwald's views on the nature of solution of electrolytes, chemical reactions could be explained in a very simple manner. For example: Sodium hydrate acting upon thiacetanilide would ordinarily allow us to expect the following:



But we find that a sodium compound is formed, which, according to its chemical reactions, requires the formula  $\text{C}_6\text{H}_5\cdot\text{N}:\text{C}\cdot\text{CH}_3\cdot\text{S Na}$ , and we are therefore forced to assume that a change

within the molecule has taken place. But considering that Na OH in solution is partly dissociated into its ions Na and OH, then we must write the following equation :



Many similar cases experimented upon are described in this paper and the authors formulate the following proposition : In reactions of tautomeric compounds, which take place under the influence of electrolytes, the exchange of atoms is caused by the free ions. (*Ber. d. Chem. Ges.*, 23, 253, 1890.) L. H. F.

**Determination of Vapor-Densities below the Boiling Point of the Substances Tested.** ROBERT DEMUTH and VICTOR MEYER.

The determination of vapor densities by the method of displacement of air has caused several chemists to attempt improvements by working in a part vacuum. But the simple method has thus been hampered by very complicated apparatus. The authors found a method for the determination of the vapor density of bodies which are easily decomposed by using hydrogen gas instead of air. If care is taken that the vapor of the substance tested spreads rapidly through the apparatus a degree of dilution is arrived at, which (like a partial vacuum) permits lower temperatures for the determination. Thus xylol, *e. g.*, was tested at 40 deg. below its boiling point, using common steam as a mantle. For certain chlorides of metals hydrogen cannot be used. Ethyl-ether was determined at 17° C., which was the temperature of the room. (*Ber. d. Chem. Ges.*, 23, 311, 1890.) L. H. F.

## ANALYTICAL CHEMISTRY.

**The Use of Pyrophosphate Double Salts in the Estimation and Separation of Metals by Electrolysis.** ALBANO BRAND.

It has been found that many of the metals contained in solution as double pyrophosphates can be easily separated by electrolysis. Since in this form of combination many of the solutions bear either

the addition of ammonium hydrate or carbonate without precipitation, there is the further advantage that the electrolysis may be carried on in alkaline or acid solution; chlorides, as well as sulphates and nitrates, may therefore be used.

When solutions of sodium or ammonium pyrophosphate are added to neutral solutions of metals, the resulting precipitate is soluble on addition of an excess of the reagent. If such a solution bears the further addition of ammonium hydrate, and also ammonium carbonate, it is (for brevity's sake) termed *normal*. Ammonium hydrate or ammonium carbonate solutions also dissolve the pyrophosphates of those metals, the sodium pyrophosphate solution of which will bear the addition of these reagents without precipitation. These solutions also bear the addition of ammonium oxalate without precipitating.

I.—BEHAVIOR OF METALS IN THE FORM OF DOUBLE PYROPHOSPHATE DURING ELECTROLYSIS.

1. *Nickel*.—Solutions react normal. From the alkaline pyrophosphate solution, especially that containing ammonium carbonate, nickel is easily deposited upon the cathode as a firmly adhering, whitish-gray metal. The deposition begins with a current of 0.1 c. c. of gas per minute. With a current of 2 to 3 c. c. per minute 0.2–0.3 grm. of nickel can be precipitated in twenty-four hours. The same quantity of metal can be precipitated in a few hours by a current of 20 c. c. per minute. The metal should be washed rapidly with distilled water without interruption of the electric current. Finally, wash with absolute alcohol, dry the tared dish at 100° C., cool and weigh. With weak currents through the ammonium carbonate nickel solution a light brown deposit may appear on the anode, but this soon disappears if the current is briefly interrupted.

2. *Cobalt*.—The electrolytic behavior of the pyrophosphate solution is much like that of nickel, the deposited metal having a brownish color. In some respects it behaves like iron, inasmuch as some of the metal is apt to be redissolved. The last traces are separated by a current of 15–20 c. c., and washed without interruption of the current.



3. *Iron*.—Ferric salts react normal. The pyrophosphate is white, and dissolves to a colorless solution in sodium pyrophosphate. On addition of ammonia, the solution turns brownish yellow or brownish red, according to concentration.

Ferrous salts also react normal. The green pyrophosphate solution on the addition of ammonium hydrate gradually turns brown, and after a time deposits basic salts.

The ammoniacal solutions of the double salts of iron, when subjected to electrolysis, deposit a brownish red salt of iron upon the anode, and at the same time metallic iron upon the cathode.

For the electrolytic estimation of iron, only the solution to which ammonium carbonate has been added is suitable.

Although the reduction begins with a light current, to separate the metal rapidly currents of 20–30 c. c. per m. are required.

4. *Manganese*.—The pyrophosphate is readily soluble in ammonia, less readily in sodium pyrophosphates. Ammonium carbonate also dissolves the precipitate, but the solution soon deposits a white salt. Manganese is best separated as a superoxide from the strongly ammoniacal solution. The solution should contain about 15% of strong water of ammonia.

To prepare the electrolyte, add just sufficient sodium pyrophosphate to form the double pyrophosphate, and then dissolve in the requisite amount of ammonia. Make the platinum capsule the positive electrode, and for small quantities of manganese (0.02 g. Mn in 100 c. c.) use a current of 0.1 c. c. per m. For larger amounts of Mn, begin with a light current (0.01 c. c. for 0.1 gm. Mn in 100 c. c.). Towards the end the current must not exceed 0.4 c. c. Wash only with water, and finally weigh the manganese as  $\text{Mn}_3\text{O}_4$ .

5. *Zinc*.—Solutions react normal. For the quantitative estimation the ammoniacal solution of the double salt, or better still, the solution to which ammonium carbonate has been added, is suitable for electrolysis, the metal being deposited as a zinc-gray, firmly adherent film. If much zinc is present (over 0.2 gm.) the bulk of it should be precipitated with a current of 5–10 c. c. per minute, increasing the current towards the end to 15–20 c. c. A wire anode is preferable to foil. Wash without interruption of current.

If zinc and iron occur together, the former can be precipitated completely only when the iron is present in large excess.

6. *Cadmium*.—Pyrophosphate soluble in large excess of the sodium pyrophosphate, much more readily in ammonia. Addition of ammonium carbonate causes a precipitate. For electrolysis the strongly ammoniacal pyrophosphate solution is the most suitable. Begin with a current of 2–3 c. c. ; after a few seconds reduce to .3 to 1. c. c., and after the bulk of the metal has been precipitated increase the current to 5 c. c. at the finish. The metal thus separated is dense, crystalline, and of silvery white color.

7. *Copper*.—Solutions react normal. For electrolysis the double pyrophosphate solution without further additions is the most suitable. A current of 0.1 c. c. per minute, which should be increased to 1 c. c. towards the end, precipitates the copper as a firm metallic film.

8. *Silver*.—The pyrophosphate is almost insoluble in excess of sodium pyrophosphate, but dissolves readily in ammonia or ammonium carbonate. The salt precipitated by ammonium pyroph. is soluble in excess of the reagent, and also in ammonium carbonate, but ammonium hydrate again precipitates the salt from this solution.

For electrolysis, a solution of the sodium double salt acidulated with nitric acid is the most suitable. Begin with a current of 0.01 c. c. and increase it to .2 c. c. towards the end.

9. *Mercury*.—The mercurous pyrophosphate is readily soluble in the sodium or ammonium pyrophosphate, but in these solutions addition of ammonia or ammonium carbonate causes dark gray precipitates. The mercuric pyrophosphate is insoluble in sod. pyroph., but dissolves readily in ammonia or ammonium carbonate solution.

For electrolysis the solutions of the mercuric double salts, to which ammonia or ammonium carbonate have been added, are the most suitable. Mercurous salts must first be oxidized to mercuric salts. A current of 2 c. c. per m. will deposit 1 g. of metal in 5–6 hours.

10. *Tin*.—The stannous and stannic pyrophosphates dissolve readily in the sodium or ammonium pyroph. solution and bear the

addition of ammonium carbonate; but ammonia causes precipitation. The quantitative estimation was not found satisfactory. -

11. *Chromium*.—Solutions react normal. During electrolysis the chromium oxidizes to chromic acid both in alkaline and acid solution. If Ni and Co are present with the chromic double salt in alkaline solution they (Ni and Co) are precipitated quantitatively. But if chromic acid be present from the beginning, neither Ni or Co will be deposited even with strong currents. In presence of iron in the ammonium carbonate solution, a reddish yellow salt appears on the cathode, containing iron and pyrophosphoric acid. If iron be in solution with chromic oxide, metallic iron is first deposited during electrolysis, but the deposition ceases as soon as chromic acid is formed.

12. *Lead*.—Pyrophosphate is soluble in excess of sodium pyrophosphate and the solution bears addition of ammonium carbonate, but is precipitated by ammonia. Not suitable for quantitative estimation by electrolysis.

13. *Thallium*.—Behavior of the pyrophosphates much like that of the lead salts.

14. *Bismuth*.—The pyrophosphate solution is precipitated by ammonia, but not by ammonium carbonate. For quantitative estimation add to the acid and somewhat dilute solution 4 or 5 times as much sod. pyrophosphate as is required to form double pyrophosphate. Add sufficient ammonium carbonate to make the solution alkaline, and then add 3–5 grms. of ammonium oxalate in solution. Begin with a current of 0.1 c. c. to 1 c. c., according to the quantity of Bi in solution, increasing current towards the end to 2–3 c. c. By the above method 1 gm. of Bi may be brought into solution in 200 c. c. Occasionally it is best to begin with a current of 1–2 c. c., and after a few seconds to decrease to required degree. About .25 grms. Bi may be deposited within 12 hours by beginning with a current of .5 c. c. and ending with one of 5 c. c. Towards the end of the reaction traces of superoxide are apt to appear on the anode, but these can be removed by means of conc. oxalic acid solution. The deposited bismuth is best weighed as an oxide, readily obtained by dissolving the deposit in  $\text{HNO}_3$ , evaporating, and finally igniting at a red heat. For the electrolysis use an anode of wire.

15. *Antimony*.—Ammonium carbonate is miscible with the pyrophosphate solution, but ammonia causes precipitation. From the solutions currents of .1–0.3 c. c. separate the metal quantitatively, but the deposit does not adhere firmly enough for quantitative estimation.

## II.—SEPARATIONS.

### SEPARATION OF MANGANESE FROM OTHER METALS.

The property of manganese separating as a superoxide from strongly ammonical solutions, but remaining in solution as a double manganic salt in acid solution, suggests two methods for the separation. From those metals whose salts bear the addition of ammonia the Mn may be separated as a superoxide, or in case the metals are reducible from acid solution to separate the metals first.

#### 1. Mn from Ni, Cu, Cd, Zn, Hg.

The separation of Mn from Fe and Co in the ammoniacal solution by electrolysis is not practicable. From nickel the manganese is readily separated by electrolyzing the solution of the double pyrophosphate after adding about 15% of stronger water of ammonia. An electrode of platinum wire is the most suitable.

The Mn is readily separated from copper since the latter is readily deposited from the ammonium solution by very weak currents. The platinum capsule is used as the cathode. For larger quantities of Cu or Mn the method under II., 2, is preferable.

#### 2. Mn from Cu, Cd, Hg.

Manganese is readily separated from all metals which are reduced by electrolysis in acid solutions. The separation from Fe, Ni and Co is possible, but it requires very strong currents. From Cu and Cd it is easily separated in weak sulphuric acid solutions, or from Cu and Hg in nitric acid solutions.

Acidulate the pyrophosphate solution with the requisite acid, and separate Cu with a current of 3–4 c. c.; Hg by a current of 0.2–0.5 c. c.; and Cd according to I., 6. After evaporating the bulk of the washing so as to concentrate the solution add oxalic acid to reduce the manganese to manganous salt, cool, add ammonia and deposit the manganese as superoxide by means of a weak current.

### 3. Mn from Fe and Co.

To separate iron from manganese add to the neutral solution containing this metal so large an excess of sod. pyrophosphate that the precipitate is redissolved. Add 4-8 grms. of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  in solution. Deposit the iron on an electrode of platinum wire, and as soon as deposition is complete remove and dip the electrode into distilled water and wash it. An electrode of 1.5 mm. diam. wire, having about 7-8 sq. cm. surface, and weighing 14.5 grms. was sufficient for 0.2 g. iron. If much iron is present begin with a current of 5 c. c., and finish with a 15-20 c. c. current. After the removal of the iron acidulate the solution with  $\text{H}_2\text{SO}_4$ , and reduce with  $\text{H}_2\text{C}_2\text{O}_4$ . After adding 15 conc. ammonia (Sp. Gr. .900), separate the manganese as a superoxide. The less iron there is in proportion to the manganese, the more reliable is the method.

### 4. Cd from Zn, Fe, Ni, Co.

Cadmium is separated readily from all metals not reduced in sulphuric acid solutions. By use of the double pyrophosphate, salts Zn, Fe, Ni, and Co, after the separation of the Cd, may be deposited direct by supersaturating the solution with ammonium carbonate and subjecting it to electrolysis. It is immaterial whether the sodium pyrophosphate is added before or after the separation of the Cd.

### 5. Cd from Zn, Ni, Mn.

Method the same as the above, but sodium pyrophosphate must first be added to keep the manganese from precipitating. The washings (after separation of Cd) are finally concentrated, reduced with oxalic acid, cooled, an excess of ammonia is added and the operation is proceeded with according to I., 4.

### 6. Fe, Ni, Co, Zn, from Al, Mg, Ur.

Of the alkaline earths Mg alone forms a pyrophosphate soluble in excess of the precipitant and which bears the addition of ammonium carbonate. Ammonia causes precipitation. Uranium double salts behave much like the magnesium salt. The aluminium pyrophosphate is further soluble in ammonia.

On electrolyzing the ammonium carbonate solution of the double pyrophosphates of Fe, Ni, Co, or Zn, containing also those of Al,

Mg, Ur, the former are reduced and the latter remain in solution thus enabling a separation. (*Ztschr. Anal. Chem.*, **28**, 581-605.)

J. F. G.

**Concentration of Reagents.** R. BLOCHMANN.

With the exception of the concentrated acids and of the *waters* containing  $H_2S$ ; Ba O; Ca O; Ca  $SO_4$  or Br, etc., etc., the degree of concentration of all of which requires special attention, it is well to prepare reagent solutions which shall be approximately normal.

The beginner in qualitative analysis should thus be led to avoid an excessive use of reagents. Moreover, the qualitative tests performed with such solutions will offer quantitative indications in regard to the substances found. (*Ber. d. Chem. Ges.*, **23**, 31, 1890.)

L. H. F.

**A New Gas Volumeter.** G. LUNGE.

This apparatus allows the direct measuring of gases without any further calculation or correction for temperature and pressure. The amount of nitrogen, *e. g.*, after a combustion is read directly in milligrammes and  $\frac{1}{10}$  mgrms. after proper cooling, without the use of a barometer or thermometer. (*Ber. d. Chem. Ges.*, **23**, 440, 1890.)

L. H. F.

**Separation and Quantitative Determination of Tin and Titanium.** A. HILGER and HEINRICH HAAS.

Stannic acid is separated from titanic acid by subjecting the mixture at a dull red heat to the reducing action of hydrogen. Stannic acid is reduced to metal, titanic acid is not. The reduced tin is dissolved from the mixture by means of hydrochloric acid of 20 per cent., which does not dissolve titanic acid. (*Ber. d. Chem. Ges.*, **23**, 458, 1890.)

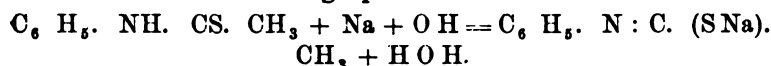
L. H. F.

**Separation of Vanadic from Tungstic Acid.** CARL FRIEDHEIM.

Berzelius' and Gibbs' methods are used jointly and with slight changes. The tungstic acid is almost quantitatively precipitated by water from hydrochloric acid solution of mercurous tungstate. (*Ber. d. Chem. Ges.*, **23**, 353, 1890.)

L. H. F.

within the molecule has taken place. But considering that Na OH in solution is partly dissociated into its ions Na and OH, then we must write the following equation :



Many similar cases experimented upon are described in this paper and the authors formulate the following proposition : In reactions of tautomeric compounds, which take place under the influence of electrolytes, the exchange of atoms is caused by the free ions. (*Ber. d. Chem. Ges.*, **23**, 253, 1890.) L. H. F.

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the addition of ammonium hydrate or carbonate without precipitation, there is the further advantage that the electrolysis may be carried on in alkaline or acid solution ; chlorides, as well as sulphates and nitrates, may therefore be used.

When solutions of sodium or ammonium pyrophosphate are added to neutral solutions of metals, the resulting precipitate is soluble on addition of an excess of the reagent. If such a solution bears the further addition of ammonium hydrate, and also ammonium carbonate, it is (for brevity's sake) termed *normal*. Ammonium hydrate or ammonium carbonate solutions also dissolve the pyrophosphates of those metals, the sodium pyrophosphate solution of which will bear the addition of these reagents without precipitation. These solutions also bear the addition of ammonium oxalate without precipitating.

#### I.—BEHAVIOR OF METALS IN THE FORM OF DOUBLE PYROPHOSPHATE DURING ELECTROLYSIS.

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2. *Cobalt*.—The electrolytic behavior of the pyrophosphate solution is much like that of nickel, the deposited metal having a brownish color. In some respects it behaves like iron, inasmuch as some of the metal is apt to be redissolved. The last traces are separated by a current of 15–20 c. c., and washed without interruption of the current.



3. *Iron*.—Ferric salts react normal. The pyrophosphate is white, and dissolves to a colorless solution in sodium pyrophosphate. On addition of ammonia, the solution turns brownish yellow or brownish red, according to concentration.

Ferrous salts also react normal. The green pyrophosphate solution on the addition of ammonium hydrate gradually turns brown, and after a time deposits basic salts.

The ammoniacal solutions of the double salts of iron, when subjected to electrolysis, deposit a brownish red salt of iron upon the anode, and at the same time metallic iron upon the cathode.

For the electrolytic estimation of iron, only the solution to which ammonium carbonate has been added is suitable.

Although the reduction begins with a light current, to separate the metal rapidly currents of 20–30 c. c. per m. are required.

4. *Manganese*.—The pyrophosphate is readily soluble in ammonia, less readily in sodium pyrophosphates. Ammonium carbonate also dissolves the precipitate, but the solution soon deposits a white salt. Manganese is best separated as a superoxide from the strongly ammoniacal solution. The solution should contain about 15% of strong water of ammonia.

To prepare the electrolyte, add just sufficient sodium pyrophosphate to form the double pyrophosphate, and then dissolve in the requisite amount of ammonia. Make the platinum capsule the positive electrode, and for small quantities of manganese (0.02 g. Mn in 100 c. c.) use a current of 0.1 c. c. per m. For larger amounts of Mn, begin with a light current (0.01 c. c. for 0.1 gm. Mn in 100 c. c.). Towards the end the current must not exceed 0.4 c. c. Wash only with water, and finally weigh the manganese as  $\text{Mn}_3\text{O}_4$ .

5. *Zinc*.—Solutions react normal. For the quantitative estimation the ammoniacal solution of the double salt, or better still, the solution to which ammonium carbonate has been added, is suitable for electrolysis, the metal being deposited as a zinc-gray, firmly adherent film. If much zinc is present (over 0.2 gm.) the bulk of it should be precipitated with a current of 5–10 c. c. per minute, increasing the current towards the end to 15–20 c. c. A wire anode is preferable to foil. Wash without interruption of current.

If zinc and iron occur together, the former can be precipitated completely only when the iron is present in large excess.

6. *Cadmium*.—Pyrophosphate soluble in large excess of the sodium pyrophosphate, much more readily in ammonia. Addition of ammonium carbonate causes a precipitate. For electrolysis the strongly ammoniacal pyrophosphate solution is the most suitable. Begin with a current of 2–3 c. c.; after a few seconds reduce to .3 to 1. c. c., and after the bulk of the metal has been precipitated increase the current to 5 c. c. at the finish. The metal thus separated is dense, crystalline, and of silvery white color.

7. *Copper*.—Solutions react normal. For electrolysis the double pyrophosphate solution without further additions is the most suitable. A current of 0.1 c. c. per minute, which should be increased to 1 c. c. towards the end, precipitates the copper as a firm metallic film.

8. *Silver*.—The pyrophosphate is almost insoluble in excess of sodium pyrophosphate, but dissolves readily in ammonia or ammonium carbonate. The salt precipitated by ammonium pyroph. is soluble in excess of the reagent, and also in ammonium carbonate, but ammonium hydrate again precipitates the salt from this solution.

For electrolysis, a solution of the sodium double salt acidulated with nitric acid is the most suitable. Begin with a current of 0.01 c. c. and increase it to .2 c. c. towards the end.

9. *Mercury*.—The mercurous pyrophosphate is readily soluble in the sodium or ammonium pyrophosphate, but in these solutions addition of ammonia or ammonium carbonate causes dark gray precipitates. The mercuric pyrophosphate is insoluble in sod. pyroph., but dissolves readily in ammonia or ammonium carbonate solution.

For electrolysis the solutions of the mercuric double salts, to which ammonia or ammonium carbonate have been added, are the most suitable. Mercurous salts must first be oxidized to mercuric salts. A current of 2 c. c. per m. will deposit 1 g. of metal in 5–6 hours.

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addition of ammonium carbonate; but ammonia causes precipitation. The quantitative estimation was not found satisfactory. -

11. *Chromium*.—Solutions react normal. During electrolysis the chromium oxidizes to chromic acid both in alkaline and acid solution. If Ni and Co are present with the chromic double salt in alkaline solution they (Ni and Co) are precipitated quantitatively. But if chromic acid be present from the beginning, neither Ni or Co will be deposited even with strong currents. In presence of iron in the ammonium carbonate solution, a reddish yellow salt appears on the cathode, containing iron and pyrophosphoric acid. If iron be in solution with chromic oxide, metallic iron is first deposited during electrolysis, but the deposition ceases as soon as chromic acid is formed.

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14. *Bismuth*.—The pyrophosphate solution is precipitated by ammonia, but not by ammonium carbonate. For quantitative estimation add to the acid and somewhat dilute solution 4 or 5 times as much sod. pyrophosphate as is required to form double pyrophosphate. Add sufficient ammonium carbonate to make the solution alkaline, and then add 3–5 grms. of ammonium oxalate in solution. Begin with a current of 0.1 c. c. to 1 c. c., according to the quantity of Bi in solution, increasing current towards the end to 2–3 c. c. By the above method 1 gm. of Bi may be brought into solution in 200 c. c. Occasionally it is best to begin with a current of 1–2 c. c., and after a few seconds to decrease to required degree. About .25 grms. Bi may be deposited within 12 hours by beginning with a current of .5 c. c. and ending with one of 5 c. c. Towards the end of the reaction traces of superoxide are apt to appear on the anode, but these can be removed by means of conc. oxalic acid solution. The deposited bismuth is best weighed as an oxide, readily obtained by dissolving the deposit in  $\text{HNO}_3$ , evaporating, and finally igniting at a red heat. For the electrolysis use an anode of wire.

15. *Antimony*.—Ammonium carbonate is miscible with the pyrophosphate solution, but ammonia causes precipitation. From the solutions currents of .1–0.3 c. c. separate the metal quantitatively, but the deposit does not adhere firmly enough for quantitative estimation.

## II.—SEPARATIONS.

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#### 1. Mn from Ni, Cu, Cd, Zn, Hg.

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The Mn is readily separated from copper since the latter is readily deposited from the ammonium solution by very weak currents. The platinum capsule is used as the cathode. For larger quantities of Cu or Mn the method under II., 2, is preferable.

#### 2. Mn from Cu, Cd, Hg.

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Acidulate the pyrophosphate solution with the requisite acid, and separate Cu with a current of 3–4 c. c.; Hg by a current of 0.2–0.5 c. c.; and Cd according to I., 6. After evaporating the bulk of the washing so as to concentrate the solution add oxalic acid to reduce the manganese to manganous salt, cool, add ammonia and deposit the manganese as superoxide by means of a weak current.

### 3. Mn from Fe and Co.

To separate iron from manganese add to the neutral solution containing this metal so large an excess of sod. pyrophosphate that the precipitate is redissolved. Add 4-8 grms. of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  in solution. Deposit the iron on an electrode of platinum wire, and as soon as deposition is complete remove and dip the electrode into distilled water and wash it. An electrode of 1.5 mm. diam. wire, having about 7-8 sq. cm. surface, and weighing 14.5 grms. was sufficient for 0.2 g. iron. If much iron is present begin with a current of 5 c. c., and finish with a 15-20 c. c. current. After the removal of the iron acidulate the solution with  $\text{H}_2\text{SO}_4$ , and reduce with  $\text{H}_2\text{C}_2\text{O}_4$ . After adding 15 conc. ammonia (Sp. Gr. .900), separate the manganese as a superoxide. The less iron there is in proportion to the manganese, the more reliable is the method.

### 4. Cd from Zn, Fe, Ni, Co.

Cadmium is separated readily from all metals not reduced in sulphuric acid solutions. By use of the double pyrophosphate, salts Zn, Fe, Ni, and Co, after the separation of the Cd, may be deposited direct by supersaturating the solution with ammonium carbonate and subjecting it to electrolysis. It is immaterial whether the sodium pyrophosphate is added before or after the separation of the Cd.

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Method the same as the above, but sodium pyrophosphate must first be added to keep the manganese from precipitating. The washings (after separation of Cd) are finally concentrated, reduced with oxalic acid, cooled, an excess of ammonia is added and the operation is proceeded with according to I., 4.

### 6. Fe, Ni, Co, Zn, from Al, Mg, Ur.

Of the alkaline earths Mg alone forms a pyrophosphate soluble in excess of the precipitant and which bears the addition of ammonium carbonate. Ammonia causes precipitation. Uranium double salts behave much like the magnesium salt. The aluminium pyrophosphate is further soluble in ammonia.

On electrolyzing the ammonium carbonate solution of the double pyrophosphates of Fe, Ni, Co, or Zn, containing also those of Al,

Mg, Ur, the former are reduced and the latter remain in solution thus enabling a separation. (*Ztschr. Anal. Chem.*, **28**, 581-605.)  
J. F. G.

**Concentration of Reagents.** R. BLOCHMANN.

With the exception of the concentrated acids and of the *waters* containing  $H_2S$ ; Ba O; Ca O; Ca  $SO_4$  or Br, etc., etc., the degree of concentration of all of which requires special attention, it is well to prepare reagent solutions which shall be approximately normal.

The beginner in qualitative analysis should thus be led to avoid an excessive use of reagents. Moreover, the qualitative tests performed with such solutions will offer quantitative indications in regard to the substances found. (*Ber. d. Chem. Ges.*, **23**, 31, 1890.)  
L. H. F.

**A New Gas Volumeter.** G. LUNGE.

This apparatus allows the direct measuring of gases without any further calculation or correction for temperature and pressure. The amount of nitrogen, *e. g.*, after a combustion is read directly in milligrammes and  $\frac{1}{10}$  mgrms. after proper cooling, without the use of a barometer or thermometer. (*Ber. d. Chem. Ges.*, **23**, 440, 1890.)  
L. H. F.

**Separation and Quantitative Determination of Tin and Titanium.** A. HILGER and HEINRICH HAAS.

Stannic acid is separated from titanic acid by subjecting the mixture at a dull red heat to the reducing action of hydrogen. Stannic acid is reduced to metal, titanic acid is not. The reduced tin is dissolved from the mixture by means of hydrochloric acid of 20 per cent., which does not dissolve titanic acid. (*Ber. d. Chem. Ges.*, **23**, 458, 1890.)  
L. H. F.

**Separation of Vanadic from Tungstic Acid.** CARL FRIEDHEIM.

Berzelius' and Gibbs' methods are used jointly and with slight changes. The tungstic acid is almost quantitatively precipitated by water from hydrochloric acid solution of mercurous tungstate. (*Ber. d. Chem. Ges.*, **23**, 353, 1890.)  
L. H. F.

**Determinations of Sulphur in Albumin free from Ash.**  
ERICH HARNACK.

The preparation and the properties of ash-free albumin have already been described. (*Ber.*, **16**, 1889.) The sulphur determinations have now been repeated. It has been found recently that the *old* method for determining sulphur in albumin bodies is the only reliable one, viz., carefully melting them with caustic alkali and  $\text{KNO}_3$ , eventually using Hammarsten's modification, consisting in a previous destruction through conc.  $\text{HNO}_3$ . The caustic potash should be prepared from potassium, since the commercial hydrates (*alcohol depuratum*) contain sulphur.

A true formula for albumin cannot yet be obtained. But the average of five analyses shows 1.91% of sulphur, while Loew's formula:  $(\text{C}_{210} \text{H}_{330} \text{N}_{52} \text{O}_{66} \text{S}_3)$  which is three times that of Lieberkühn, requires 2.03% of sulphur. This is a close approximation. Finally, the author draws attention to the fact that the ratios of sulphur to carbon in the three substances: egg albumin, globulin from pumpkin seed and hæmoglobin are as 1:2:5. (*Ber. d. Chem. Ges.*, **23**, 40, 1890.)

L. H. F.

**Quantitative Determination of Egg Substance.** S. BEIN.

Yolk of egg contains two substances, the glycerine phosphoric acid and lecithin, both of which are soluble in ether. The lecithin is an ether of distearyl-glycerinphosphate with neurine. According to Gobley, the egg yolk contains 7.2 per cent. lecithine and 1.2 per cent. glycerine phosphoric acid. Taking into consideration the formulæ of these two compounds, the determination of phosphoric acid in the ash of the ethereal extract admits of a quantitative determination. The presence of 1.12902 grms. of phosphoric acid would indicate 100 grms. of yolk of egg. This analysis is applied in forensic cases. (*Ber. d. Chem. Ges.*, **23**, 423, 1890.)

L. H. F.

## Abstracts of American Patents Relating to Chemistry.

(From the U. S. Patent Office Gazette.)

(Issued April 29th, 1890.)

**426,489.**—Filter. W. Connolly.

**426,504.**—Laundry blue. G. R. B. Kempton.

Consists of a saturated solution of alum, sodium chloride, and color soluble in water.

**426,513.**—Composition of matter for making billiard balls, combs, etc. J. H. Patterson.

Consists of zinc white, shellac, camphor, alcohol, nitrogenized rags and French chalk with glycerine, castor oil and alcohol.

**426,519.**—Artificial fuel. E. K. Baeyerlin.

Consists of coal, wood charcoal, sodium carbonate, sodium nitrate, nitric acid, potassium chloride, manganese dioxide, potassium permanganate, borax, held together by a suitable binding material.

**426,633.**—Waterproofing composition for paper. H. J. Bird.

Consists of petroleum residuum, known as "tailing," the pitch from distillation of petroleum, and asphalt.

**426,643.**—Process of manufacturing porous earthenware. W. Lenderoth.

The process consists in subjecting a mixture of clay, sand, sawdust and lime first to such a degree of heat as will reduce the sawdust to ashes and will combine said ashes with the heated lime into a flux, and in afterward increasing the temperature to cause said flux of lime and ashes to incrust and vitrify around the cells without at the same time vitrifying the mixture of clay and sand.

**426,756.**—Water filter. H. J. Becker.

**426,820.**—Glass melting pot. E. Kaye.

**426,823.**—Apparatus for manufacturing gas. G. Leisner.

**426,897.**—Welding compound. C. Wrigley.

Consists of borax, ammonium chloride and resin.

**426,933.**—Process of manufacturing antiseptic paper. A. Grossich and P. Matcovich.

**426,945.**—Filter. P. A. Maignen.

**426,965.**—Beer filtering apparatus. P. Seibel.

**426,982.**—System of filtration of water for city or town supplies. J. A. Crocker.

**426,995.**—Beer filtering apparatus. J. W. Hyatt.



*(Issued May 6th, 1890.)***427,167.**—Heat insulating compound. N. C. Fowler.

Consists of sifted or lixiviated ashes, calcium carbonate, finely divided combustible fibre, lampblack and pumice stone.

**427,187.**—Photographic or laboratory lamp. H. G. Ramsperger.**427,197.**—Carburetor. W. H. Shannon.**427,225.**—Carburetor. J. J. Cooper.**427,236.**—Filtering apparatus. W. M. Jewell.**427,379.**—Gas burner. E. F. Trent.**427,410.**—Process of extracting oil. W. T. Forbes.

The process consists in treating oleaginous material with a solvent, then expelling the dissolved oil and solvent from the mass by centrifugal force, then introducing steam to vaporize any of the solvent remaining in the residuum, then drying the same by applying centrifugal force, all of the different steps of the process being applied while the material operated upon is contained in the revolving chamber of a centrifugal machine.

**427,467.**—Obtaining chlorine. R. Dormer.

The process consists in adding to the manganese dioxide or Weldon mud only one-half the usual quantity of hydrochloric acid used in the Weldon process, and also sufficient sulphuric acid to convert into sulphates all the compounds of manganese and lime present, and then adding sufficient calcium chloride to reconvert the manganese sulphate into chloride.

**427,487.**—Carburetor. J. S. Tibbets.*(Issued May 13th, 1890.)***427,553.**—Yeast cake. J. W. Cameron.

Dry yeast is preserved by it forming into cakes or balls, each of which is first coated with sugar, and then with some innocuous waterproof substance.

**427,564.**—Carbonic acid compound of metaamidophenol. R. Guehm and J. Schmid.**427,565.**—Carbonic acid compound of dimethyl metaamidophenol. R. Guehm and J. Schmid.**427,591.**—Wall covering composition. R. B. Martin and E. H. Martin.

Consists of citric acid, sulphurate of lime, sand and water.

**427,595.**—Hydrocarbon burner. W. S. More.**427,620.**—Obtaining permanent hydroquinone. K. Scholz.

Hydrochinone is crystallized from a solution containing sulphuric acid.

**427,626.**—Apparatus for making vinegar. C. W. Shedd.**427,654.**—Glass furnace. J. B. Archer.**427,679.**—Dynamite. P. Germain.

Uses spongy vegetable matter—such as the pith of elder and other plants, the porous part of cocoanut husks, spongy agaric or the like—for holding nitroglycerin. This spongy matter is rasped and boiled in an alkaline solution, separated by levigation, washed, and dried.

**427,697.**—Apparatus for dyeing hides. J. Kristen.

**427,707.**—Mixer for explosives. W. R. Quinan.

**427,721.**—Barrel lining. A. Zinsser.

Consists of deodorized copal, resin, india rubber, a non-drying fat, with coloring matter, such as asphalt.

**427,744.**—Process of obtaining chlorine compounds from natural gas. T. F. Colin.

Chlorine and natural gas or methane are mixed within a chamber or retort, which is maintained at a proper temperature. The gases are ignited and the reaction is kept up by an electric spark of proper tension. The hydrochloric acid is then absorbed, and the methyl chloride liquefied.

**427,747.**—Apparatus for the manufacture of gas. W. M. Cosh.

**427,765.**—Ice machine and method of operating same. W. T. Hildrup, Jr., and T. H. Butler.

**427,779.**—Food compound or condiment. M. B. Manwaring.

Consists of diastase and salt.

**427,786.**—Welding compound. H. S. McLeod.

Consists of borax, salt, and iron chips or filings.

**427,794.**—Filter press. B. Remmers.

**427,819.**—Hydrocarbon burner. J. Adams.

**427,820.**—Hydrocarbon burner. J. Adams.

**427,832.**—Carbureting apparatus. G. H. Burrows.

**427,892.**—Method of lining boilers, etc., with lead. G. R. Noble.

A layer of tin is interposed between the iron and lead.

**427,906.**—Filter. C. G. Purdy.

**427,946.**—Hydrocarbon burner. J. Adams.

**427,969.**—Welding compound. W. G. Clark.

A flux for uniting copper to other metals, consisting of silicious sand, ferric oxide, alumina and calcium carbonate.

**428,015.**—Incrustation preventive. J. W. Mitchell.

Consists of soda ash, pure mineral oil, oil of pennyroyal, copper sulphate and tannin.

**428,017.**—Process of making white lead. A. Orr.

The process consists in mixing litharge and water in about equal proportions, with a small quantity of acetic acid, in about the proportion of one pound or less of acetic acid for every hundred pounds of lead oxide, injecting carbon dioxide into the mixture, and at the same time agitating the latter.

(Issued May 20th, 1890.)

**428,087.**—Process of electro-deposition. D. Garrett.

The process consists in first making a mold or matrix of a metal or alloy fusible at a lower temperature than either of the metals to be deposited; second, depositing a thin film of bright metal on the matrix or mold; third, depositing the precious metal on said thin film of bright metal; fourth, depositing the base metal deposit on said coating of precious metal; fifth, melting away the fusible mold or matrix, and finally removing the preparatory film of bright metal by buffing.

**428,101.**—Apparatus for extracting hops. J. Irlbacker.

**428,114.**—Welding compound. A. D. Le Roy and C. A. Lowell.

Consists of heating furnace cinder, iron drillings and borax.

**428,121.**—Apparatus for manufacturing salt. A. Miller.

**428,125.**—Gas holder. A. Newell.

**428,127.**—Gas holder. A. Newell.

**428,146.**—Process of producing indelible aniline ink. J. Schiffmann.

Consists in causing the slow oxidation of a mixture of aniline oil and hydrochloric acid by an oxidizing agent, while the bases are in excess of the acid, dissolving the violet coloring matter produced in an acid, and filtering.

**428,161.**—Preserving compound. J. R. Bate and F. W. Owen.

Consists of sulphur, carbon, borax, sodium chloride, and calcium chloride, in combination with suitable means for combustion thereof, and the bringing of the fumes or gases of such combustion in contact with the animal body to be preserved.

**428,162.**—Filter. E. Bourne.

**428,219.**—Composition of matter. A. J. McDarmel.

Is to be used in making manifold manuscript copies, and consists of glycerin, oxalic acid, alcohol, white glue, carbolic acid, water and gum arabic.

**428,237.**—Gas producer. W. J. Taylor.

**428,281.**—Evaporating apparatus. A. Miller.

**428,282.**—Process of manufacturing salt. A. Miller.

**428,286.**—Phenyldihydroquinazoline. C. Paal.

Medical compound having the formula  $C_{14}H_{12}N_2$ .

**428,408.**—Process of making bleaching powder and caustic soda. J. D. Pennock and J. A. Bradburn.

The process is as follows: First, salt is heated in a still by steam or its equivalent with nitric acid; second, the resulting gases, nitrosyl chloride and chlorine, are passed through a vessel containing nitric acid and manganese dioxide, the resulting gas, chlorine, being passed through a washer, and then to the bleaching powder chamber; third, the nitric acid in the sodium nitrate is recovered by furnacing with oxide of iron, and the mix-

ture lixiviated to recover caustic soda; the nitric acid in the manganese nitrate is recovered by heat, and the manganese dioxide used over again.

**428,456.**—Apparatus for compressing air or other gases. E. F. Clarke.

**428,468.**—Process of recovering glycerin from spent soap lye. A. Domeyer and O. C. Hagemann.

**428,469.**—Apparatus for concentrating spent soap lye. A. Domeyer and O. C. Hagemann.

**428,470.**—Apparatus for the distillation of concentrated soap lye. A. Domeyer and O. C. Hagemann.

**428,471.**—Process of distilling glycerin recovered from spent soap lye. A. Domeyer and O. C. Hagemann.

**428,484.**—Process of purifying glycerin. O. C. Hagemann.

**428,486.**—Washing compound. E. Hand.

Consists of paraffin wax, sperm oil, alcohol and oil of mirbane.

**428,509.**—Process of recovering glycerine from spent soap lye. E. K. Mitting.

The lye is neutralized with acid and concentrated until it is saturated with salts, after which it is treated with cellulose or equivalent fibrous or cellular substance, and an excess of acid, and filtered to remove the precipitated impurities. It is then neutralized with an alkali and concentrated.

**428,510.**—Process of recovering glycerin from spent soap lye. E. K. Mitting.

**428,530.**—Rosinduline monosulpho acid. C. Schraube.

**428,566.**—Treatment of metallic precipitates. E. K. Mitting.

W. R.



REGULAR MEETING, JUNE 6th, 1890.

Vice-President Breneman in the chair.

The minutes of the meetings of May 12th and 16th were read and accepted.

Mr. Chas. A. Catlin of the Rumford Chemical Works, Providence, R. I., and Mr. Ernest J. Lederle, Ph. B., of Stapleton, S. I., were elected as members, and D. F. Lucas, M. D., of Brooklyn, was elected as associate member.

The following were proposed as members: Chas. A. Pitkin, A. M., Ph. D., College of Physicians and Surgeons, Boston, Mass.; Geo. W. Patterson, Torpedo Station, Newport, R. I.; Major W. R. Livermore, Engineering Corps, U. S. A., Newport, R. I.; Lewis H. Laudy, Ph. D., School of Mines, New York.

Drs. Hale and Kent and Mr. Geisler were appointed as a committee to open and count the ballots on the revision of the Constitution received by the Corresponding Secretary.

Dr. Hale announced the result as follows: Seventy-three ballots had been received, two of which were thrown out as irregular.

Of the 71 regular ballots, 50 were for the new Constitution, 16 for the new Constitution without the fellowship clauses, and five against the Constitution.

The chair therefore declared the new Constitution accepted, as presented, by a clear majority vote.

A committee of three, consisting of Dr. Hale, Mr. McKenna and Mr. Geisler was appointed to ascertain the sense of the Society upon the question of holding an annual dinner, and was instructed to report at the October meeting.

The resignation of Mr. J. I. Holly was read and accepted.

Upon a motion of Dr. Munsell, the Board of Directors were empowered, at their discretion, to call a meeting of the Society in August or September in some city other than New York.

Dr. Waller read a paper "On the Determination of Lithia in Mineral Waters," after which the meeting was adjourned.

CHAS. F. MCKENNA,  
Recording Secretary.

# REVISED CONSTITUTION OF THE AMERICAN CHEMICAL SOCIETY.\*

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## ARTICLE I.

### NAME.

This Society shall be known as the AMERICAN CHEMICAL SOCIETY.

## ARTICLE II.

### OBJECTS.

The objects of the Society shall be the advancement of Chemistry and the promotion of chemical research.

## ARTICLE III.

### MEMBERSHIP.

*Section 1.* The Society shall consist of Members, Associates, Fellows and Honorary Members.

*Section 2.* Any person who has conducted an original scientific research in chemistry, and published the result thereof, or who has received a degree in chemistry from an institution of repute, or who has taught chemistry in such an institution, or who has been engaged as a chemist in technical pursuits, shall be eligible for membership.

*Section 3.* Students of chemistry and all others interested in the objects which the Society seeks to promote, shall be eligible for election as Associates. Associates shall have all the privileges of members, except the rights of voting, holding office or serving on committees.

*Section 4.* Any member in good standing who has contributed an original article to the Journal of the Society shall be eligible for election as a Fellow.

*Section 5.* Past Presidents shall be *ex-officio* Fellows so long as they remain connected with the Society.

*Section 6.* Candidates for fellowship, not Past Presidents, shall be elected only by a majority vote of the Board of Directors, after

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\*Adopted June 6, 1890.

the presentation of their names to the Board, endorsed by ten members of the Society, not more than three of whom shall be Directors.

*Section 7.* Any member, not in arrears, paying at any one time the sum of one hundred dollars into the treasury of the Society, as commutation for dues, shall become a Life Member and shall be exempt from the further payment of annual dues.

#### ARTICLE IV.

##### OFFICERS.

*Section 1.* The officers of the Society shall be elected annually. They shall be

A President,  
Six Vice-Presidents,  
A Corresponding Secretary,  
A Recording Secretary,  
A Treasurer,  
A Librarian,  
Three Curators,

and a Board of thirteen Directors.

*Section 2.* The Board of Directors shall consist of the President, the three local Vice-Presidents, the Corresponding Secretary, the Recording Secretary, the Treasurer and six other members or Fellows of the Society. Any of the other officers may be members of the Board of Directors, if elected as such at the annual meeting.

#### ARTICLE V.

##### ADVISORY COUNCIL.

At the first annual meeting after the adoption of this Article there shall be elected twelve members of the Society, not more than three of whom shall reside within fifty miles of the City of New York, who, together with the President of the Society and the Chairmen of Local Sections, shall constitute an Advisory Council.

Of the twelve members of the Council first elected four shall be elected to serve for one year, four for two years and four for



three years, and after the annual meeting at which the Council is first elected four members shall be elected at each annual meeting to serve for three years to replace those members whose terms of office expire.

The Council shall be consulted in framing amendments to the Constitution or By-Laws, in the selection of places for the holding of general meetings, and in the expenditure of money from the General Fund, whenever such expenditure shall exceed five hundred dollars for any one purpose, and shall act as an advisory body in all matters affecting the general policy of the Society. Advice or suggestions offered by members of the Council upon any measures which come within their province shall be formally presented at the meeting of the Board of Directors, or of the Society, as the case may be, before action is taken upon such measures.

The President of the Society shall be President of the Advisory Council, *ex-officio*.

## ARTICLE VI.

### STANDING COMMITTEES.

There shall be

1. A Committee on Nominations for membership, consisting of five members ;
2. A Committee on Papers and Publications, consisting of three members.

## ARTICLE VII.

### MEETINGS.

*Section 1.* The annual meeting for the election of officers and committees shall be held in the month of December in each year, at the headquarters of the Society, and a majority of the votes cast shall be necessary for an election.

*Section 2.* General meetings may be held elsewhere at the pleasure of the Society.

## ARTICLE VIII.

### VOTING.

At the annual meeting of the Society and in voting for amendments to the Constitution and By-Laws, any absent member may

vote by a ballot subscribed with his own name, or may give authority in writing to any member to act as his proxy in voting.

#### ARTICLE IX.

##### HEADQUARTERS.

The headquarters of the Society shall be in the City of New York, and ten members shall constitute a quorum.

#### ARTICLE X.

##### LOCAL SECTIONS.

Local Sections of the Society, may be established by the Board of Directors on the receipt of a written request to that effect signed by ten members of the Society in good standing and not residing within fifty miles of the City of New York.

Such Sections may appoint their own local officers and committees, and may make any rules for their government not inconsistent with the Constitution and By-Laws of the Society. They may receive for local uses a share of their annual dues to the Society as provided in Art. XI.

The chairman of each Local Section shall be, *ex-officio*, a member of the Advisory Council.

Any Local Section may be dissolved by the Board of Directors.

#### ARTICLE XI.

##### FINANCES.

*Section 1.* All moneys received as annual dues of resident or subscription members shall be applicable as follows :

*Two-thirds* to the publication of the Journal and the general operating expenses of the Society.

*One-third*, or so much thereof as may be desired, in payment of rent or for other local uses.

*Section 2.* Any moneys from the above sources, not required for the Journal or for the general operating expenses and all surplus moneys not otherwise provided for shall be invested by the Board of Directors for the benefit of the Society within one year. Moneys so invested shall constitute the General Fund of the Society, and shall be so designated.

*Section 3.* Donations and bequests of money may be received, and expended or invested as hereinbefore provided, at the discretion of the respective governing bodies.

*Section 4.* All interest accruing from the invested funds of the Society may be reinvested or expended for the publication of the Journal, or for the general operating expenses of the Society, provided, however, that all interest, other than that derived from life memberships, as well as the General Fund, may be devoted, in whole or in part, to any special object, as determined by a majority of ballots cast in a general vote of the Society.

*Section 5.* All moneys received for life membership shall be invested as soon as possible and shall constitute a trust fund, to be known as the "Life Membership Fund," which shall be held in perpetuity to guarantee the future interests of such life members. The interest of said fund may, however, be employed in the publication of the Journal, but for no other purpose.

*Section 6.* All investments of the funds of the Society shall be made only in registered United States Government Bonds.

*Section 7.* All the provisions of Sections 1 and 2 of this Article shall apply equally to the Society and to all Local Sections.

## ARTICLE XII.

### AMENDMENTS TO THE CONSTITUTION.

Amendments to the Constitution shall be presented by the Board of Directors to the Society, upon the request of fifteen members, at the next regular meeting after the receipt of such request.

A copy of the proposed amendment shall be mailed within ten days thereafter to the address of each member. The amendment or amendments shall be voted upon at the following regular meeting. The assent of two-thirds of the members voting upon an amendment shall be necessary to its adoption.

## ON BLAST FURNACE SLAGS AND THE FUSIBILITY OF SILICATES.

BY AUGUSTE J. ROSSI.

Blast furnace slags are, with pig iron, the ultimate products of the reduction of the charges, their composition depending on the proportion of the different earthy elements contained in the ashes of coal, in the limestone and the ores, at least, of such elements as can form fusible compounds. As such, they are the real criterion by which a skillful manager will judge of the economical running of his furnace.

In general, other things being equal, the composition of the slags directly affects their fusibility and bears a close relation to the grade of iron obtained. Certain conditions corresponding to a comparatively low temperature in the furnace require also a very fusible slag and a readily fusible iron. Within certain limits, to be mentioned later, such a temperature may be sufficient to melt slags of a somewhat different composition, and that slag which requires the fusion of the least quantity of foreign matters, will be, obviously, the most economical and advantageous. Works on metallurgy contain many analyses of slags, often of little value, because neither the composition of the materials charged, their relative proportion, nor the character of the resulting pig metal are mentioned. There is no way of deducing—from the composition of the slag—its economy under given conditions. A blast furnace is as much a chemical apparatus as any that is used. Chemical laws govern the reactions which take place in it and metallurgists often find in practice that the composition of slags calculated from known charges, agree almost as closely as duplicate analyses. It is very desirable that all analyses of slags published should be accompanied by the data pertaining to each case. The writer has collected the analyses of a great number of slags from European and American furnaces, many made by himself; with most of them he has been able to ascertain the accompanying conditions, and in all the general conditions and the character at least

of the pig metal run with them are known. It has seemed to him that some information on a subject so important for iron workers would be of interest.

The works of Berthier, Caron, Ebelmen, Percy and others, on the fusibility of silicates, have been precious contributions to this question, but they are not generally well known to those who would find them most useful, owing perhaps to the preconceived idea that they are too technical. It is intended to quote from them practical data exclusively, showing, by a few examples, that the conclusions which these metallurgists have reached are fully corroborated by blast furnace practice. The present paper will be limited to the subject of fusibility of silicates so far as connected with their composition, with economy of working and character of pig metal. Many circumstances may modify results sometimes foreseen, and to say that a slag of a certain composition and fusibility will invariably correspond to a stated grade of iron is impossible. Still, it will be found that divergences, when well marked and decided, can generally be traced to certain special or abnormal conditions.

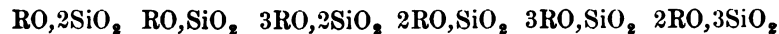
The determination of the empirical or rational formula of a silicate presents no difficulty to the technical chemist, but it involves a kind of knowledge which many iron masters, otherwise thoroughly competent, do not always have at command. Slags are complex silicates, principally of alumina, lime and magnesia, but contain also, and normally, notable percentages of ferrous and manganous oxide, potash, soda and baryta, amounting to as much as 7 and 8 per cent. The presence of these elements in quantities which cannot be neglected in ascertaining the type of a silicate, still further complicates the calculations. The composition of a slag, the percentage of its constituents, rarely affords, at first sight, a clear conception of its chemical character. A comparison with others, if it can be easily made, may be of great advantage. Given the percentage of silica and of the different bases, by a simple calculation and a table given below, without the use of any *chemical symbol or formula*, the character of a slag, its approximation to a certain chemical type, can be ascertained at once. The method is given in full.

Blast furnace slag is a combination of silica with various bases, principally alumina, magnesia and lime. The ores of iron contain, as gangue, silica associated with certain earthy or alkaline bases and almost invariably an excess of free silica as quartz. Should such an ore be smelted without any addition of fluxes, the free silica, not finding a base, would combine with a part of the oxide of iron which it would remove as slag. This is what takes place in the Catalan forge, where the slag is obtained at the sacrifice of a certain quantity of iron. Fluxes are then added in the form of limestone or dolomitic limestone, of which as little should be used as is consistent with the proper fusibility of the silicate formed from the silica of the ores and the ash of the coal with the bases found in the latter and in the limestone.

Owing to the complexity of the silicates as compounds, the theory of them is still obscure and, in the following, we do not pretend to deal with theoretical considerations, but only with slags as they appear in books on metallurgy and as they are practically known to ironmasters.

In the composition of slags as given in these works, up to a comparatively recent date, the symbol  $\text{SiO}_3$  is used for silica, which was for a long time regarded as a "trioxide." The *equivalent* of silicon was then taken at 22.00 by some, at 21.25 by others; it is now assumed to be 14.00; at. wt. Si = 28.00. The equivalent of silica,  $\text{SiO}_3$ , was consequently taken as 46.00 or 45.25 as the case might be, that of  $\text{SiO}_2$  is now 30, mol. wt. 60. The oxygen of silica calculated from the old formula  $\text{SiO}_3$  was then:  $\frac{2}{3} \times 25 = 0.530$  or  $\frac{2}{3} \times 24 = 0.522$ . It is now  $\frac{1}{2} = 0.533$ . In the same manner the *equivalents* of lime, magnesia and alumina, as late as 1865, were slightly different from what they are assumed to be now, that of lime being taken at 28.25, which is now 28.00; at. wt. 56. All these differences affect only the hundredths of the composition as given in these books.  $\text{SiO}_2$  will be used here for silica, unless otherwise mentioned. All the formulæ of slags are expressed in *equivalents*, (and not in the atomic weights) in all books up to 1886 and even later, and this practice will be followed here. Whatever may be said logically of the consideration of silicates as derivatives of certain hypothetical radicals, the use of the equiv-

alents has, in this case, the advantage of representing clearly to the eye a certain relation of silica to bases, and of the oxygen of the acid to the oxygen of the bases, corresponding, in general, to a certain grade of iron. The different earths not only saturate different quantities of silica according to their equivalents, but, for the same base, the proportions of the basic element to that of the acid may vary. The result of all observations shows that compound as well as simple bodies combine together in a certain number of proportions distinctly determined, which are generally to each other in simple ratio, at least when we deal with natural minerals. For instance, 1, 2, 3 of lime, magnesia or, in general, of such other oxides of symbol  $RO$ , will combine with the same quantity 1 of silica or conversely: so also will alumina or isomorphous oxides,  $R_2O_3$ , though in different proportions. Blast furnaces slags considered as silicates of protoxide may be: acid, neutral, sesquibasic, bibasic or, occasionally, tribasic. Sesquiacid slags correspond to "types" in which there is respectively: 1 of base to 2 of acid (acid); 1 of base to 1 of acid (neutral);  $1\frac{1}{2}$  of base to 1 of acid, or, 3 of base to 2 of acid (sesquibasic); 2 of base to 1 of acid (bibasic); 3 of base to 1 of acid (tribasic); 1 of base to  $1\frac{1}{2}$  of acid or 2 of base to 3 of acid (sesquiacid). Their formulæ are



Acid, neutral, sesquibasic, bibasic, tribasic and sesquiacid and the ratio of oxygen of the silica to that of the base is respectively for each:

4:1          2:1          4:3          1:1          2:3          6:2 or 3:1

Many other silicates fall between these types and are met with in slags. To form a neutral silicate, that is one in which the oxygen of the acid is double that of the base, the bases of the formula  $R_2O_3$ , require 3 atoms of acid. Hence, the neutral silicates in  $R_2O_3$  take the form  $R_2O_3, 3SiO_2$ ; the acid silicates, 1 base to 2 of acid, will be represented then by  $R_2O_3, 6SiO_2$ , the sesquibasic,  $1\frac{1}{2}$  base to 1 acid, by  $1\frac{1}{2}R_2O_3, 3SiO_2$ , or,  $3R_2O_3, 6SiO_2$ , or,  $R_2O_3, 2SiO_2$ , and, indeed, oxygen of acid 4, oxygen base 3::4:3. In the same manner the bibasic silicate in  $R_2O_3$  has for its formula:  $2R_2O_3, 3SiO_2$ ; the tribasic,  $R_2O_3, SiO_2$ ; the sesquiacid:  $2R_2O_3, 3SiO_2$ . If we insist on these points it is because these





TABLE I.—Continued.

NEW FORMULA : $\text{SiO}_2$ .	Corresponding to :	OLD FORMULA : $\text{SiO}_2$ .
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(B.)— <i>Sesquacid Silicate.</i> $1\frac{1}{2}$ Eq. acid to 1 base RO or 3 " to 2 " RO 9 " to 2 " $\text{R}_2\text{O}_3$ O. ratio... $\text{RO} \dots \text{R}_2\text{O}_3 \dots \text{SiO}_2$ 2 : 6 : 24 or 1 : 3 : 12 Formula... $2\text{RO} \cdot 3\text{SiO}_2 + 2\text{R}_2\text{O}_3 \cdot 9\text{SiO}_2$ O of acid : O of bases :: 12 : 4 = 3 : 1 Trisilicate derived from $\text{H}_4\text{Si}_2\text{O}_7 = 2\text{H}_2\text{O} \cdot 8\text{SiO}_2$ O ratio = 3 : 1	(B.)— <i>Neutral or Trisilicate of Percy.</i> O. ratio... $\text{RO} \dots \text{R}_2\text{O}_3 \dots \text{SiO}_2$ 1 : 3 : 12 Formula... $\text{RO} \cdot \text{SiO}_2 + \text{R}_2\text{O}_3 \cdot 3\text{SiO}_2$ O of acid : O of bases :: 12 : 4 = 3 : 1	
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(C.)— <i>Neutral Silicate.</i> 1 Equiv. acid to 1 base RO 3 " to 1 " $\text{R}_2\text{O}_3$ O. ratio... $\text{RO} \dots \text{R}_2\text{O}_3 \cdot \text{SiO}_2$ 1 : 3 : 8 Formula... $\text{RO} \cdot \text{SiO}_2 + \text{R}_2\text{O}_3 \cdot 3\text{SiO}_2$ O of acid : O of bases :: 8 : 4 = 2 : 1 The monosilicate of modern type derived from metasilicic acid $\text{H}_2\text{SiO}_3 = \text{H}_2\text{O} \cdot \text{SiO}_2$ O ratio 2 : 1	(C.)— <i>Sesquibasic or Bisilicate of Percy.</i> O. ratio... $\text{RO} \dots \text{R}_2\text{O}_3 \dots \text{SiO}_2$ 3 : 3 : 12 or 1 : 1 : 4 Formula... $3\text{RO} \cdot 2\text{SiO}_2 + \text{R}_2\text{O}_3 \cdot 2\text{SiO}_2$ O of acid : O of bases :: 4 : 2 = 2 : 1	
<hr/>		
(D.)— <i>No Special Name.</i> 3 Eq. acid to 4 of base RO 9 " to 4 " $\text{R}_2\text{O}_3$ RO O. ratio... 4 : 12 : 24 or 1 : 3 : 6 Formula... $4\text{RO} \cdot 3\text{SiO}_2 + 4\text{R}_2\text{O}_3 \cdot 9\text{SiO}_2$ O of acid : O of bases = 24 : 16 or 3 : 2 A trisilicate of modern type.	(D.)— <i>The Bibasic or Sesquisilicate of Percy.</i> O. ratio... 2 : 6 : 12 or 1 : 3 : 6 Formula... $2\text{RO} \cdot \text{SiO}_2 + 2\text{R}_2\text{O}_3 \cdot 3\text{SiO}_2$ O of acid : O of bases :: 6 : 4 = 3 : 2	
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(E.)— <i>Sesquibasic Silicate.</i> 1 acid to $1\frac{1}{2}$ base RO or 2 " to 3 " RO 6 acid to 3 base $\text{R}_2\text{O}_3$ O. ratio... 3 : 3 : 8 or 2 " to 1 " $\text{R}_2\text{O}_3$ Formula... $3\text{RO} \cdot 2\text{SiO}_2 + \text{R}_2\text{O}_3 \cdot 2\text{SiO}_2$ O of acid : O of bases : 8 : 6 = 4 : 3 A disilicate of modern type derived from $\text{H}_6\text{Si}_2\text{O}_7 = 3(\text{H}_2\text{O}) \cdot 2\text{SiO}_2$ . O ratio 4 : 3.	(E.)— <i>No special name by Percy.</i> O. ratio... $\text{RO} \dots \text{R}_2\text{O}_3 \dots \text{SiO}_2$ 9 : 9 : 24 or 3 : 3 : 8 Formula... $9\text{RO} \cdot 4\text{SiO}_2 + 3\text{R}_2\text{O}_3 \cdot 4\text{SiO}_2$ O of acid : O of bases :: 24 : 18 = 8 : 6 = 4 : 3	
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(F.)— <i>Bibasic Silicate.</i> 1 acid to 2 base RO 3 " to 2 " $\text{R}_2\text{O}_3$ O. ratio... 2 : 6 : 8 = 1 : 3 : 4 Formula... $2\text{RO} \cdot \text{SiO}_2 + 2\text{R}_2\text{O}_3 \cdot 3\text{SiO}_2$ O of acid : O of bases :: 4 : 4 = 1 : 1 The monosilicate, basic, of modern nomenclature, derived from orthosilicic acid $\text{H}_4\text{SiO}_4 = 2(\text{H}_2\text{O}) \cdot \text{SiO}_2$ : O ratio 1 : 1	(F.)— <i>Tribasic or Monosilicate of Percy.</i> O. ratio... 3 : 3 : 6 or 1 : 1 : 2 Formula... $3\text{RO} \cdot \text{SiO}_2 + \text{R}_2\text{O}_3 \cdot \text{SiO}_2$ O of acid : O of bases :: 2 : 2 = 1 : 1.	
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(G.)— <i>Tribasic Silicate.</i> 1 acid to 3 base RO 3 " to 3 " $\text{R}_2\text{O}_3$ or 1 " to 1 " $\text{R}_2\text{O}_3$ O. ratio... 3 : 3 : 4 Formula... $3\text{RO} \cdot \text{SiO}_2 + \text{R}_2\text{O}_3 \cdot \text{SiO}_2$ O of acid : O of bases :: 4 : 6 = 2 : 3 The monosilicate, <i>parasilicate</i> of modern nomenclature, derived from $\text{H}_6\text{Si}_2\text{O}_7 = 3(\text{H}_2\text{O}) \cdot \text{SiO}_2$ , O ratio 2 : 3.	(G.)— <i>No special name by Percy.</i> O. ratio... 9 : 9 : 12 or 3 : 3 : 4 Formula... $9\text{RO} \cdot 2\text{SiO}_2 + 3\text{R}_2\text{O}_3 \cdot 2\text{SiO}_2$ O of acid : O of bases :: 12 : 18 = 4 : 6 = 2 : 3	

It will be seen that the ratio of oxygen of acid to that of bases is *the same* in both formulæ, as it should be, since:  $3\text{SiO}_2 = 2\text{SiO}_3$ , as far as oxygen is concerned; and also as to total equivalent;  $3\text{SiO}_2 = 90$ , using present equivalents, or  $2 \times 45 = 90$ , using the old equivalent assumed for silicon.

This ratio of oxygen of acid to oxygen of base is the most *characteristic feature of a type of silicates*, whatever may be said of their exact molecular composition. When it is found to be *the same* in two silicates containing different bases in different proportions it corresponds to the same calculated empirical formula for each, to the same saturation of bases and acid and the same fusibility, the conditions of temperature determining the production of such slags in a blast furnace are similar, in other words, they are likely to accompany the same grade of iron.

In a question of such importance as this, involving references to works in which notations and nomenclature are different from those now used, it is necessary to establish a clear basis of understanding.

Using the symbol  $\text{SiO}_2$  for silica, Percy and others have called a *neutral silicate* or *trisilicate* a silicate in which the O of base: O of acid :: 1:3. Hence,  $\text{RO}, \text{SiO}_3$  represented for him a trisilicate. Now such silicate, with  $\text{SiO}_2$ , corresponds to a *sesquiacid* silicate  $2\text{RO}, 3\text{SiO}_2$ ; O of silica, 6: O of  $\text{RO}$ , 2 :: 3:1; the neutral silicate of our days being one in which O of acid =  $2 \times$  O of bases or  $\text{RO}, \text{SiO}_2$ , silica being a *dioxide*, not a *trioxide*. In  $\text{R}_2\text{O}_3$  this neutral silicate of Percy has the formula  $\text{R}_2\text{O}_3, 3\text{SiO}_3$  (O of silica,  $9 = 3 \times 3$  times O of base). Now:  $2\text{R}_2\text{O}_3, 9\text{SiO}_2$  (O acid  $18 =$  O base,  $6 \times 3$ ).

In the same manner he called a *sesquibasic* or *bisilicate* a silicate in which O of acid =  $2 \times$  O of bases,  $3\text{RO}, 2\text{SiO}_3$ ;  $\text{R}_2\text{O}_3, 2\text{SiO}_3$ ; now:  $\text{RO}, \text{SiO}_2 + \text{R}_2\text{O}_3, 3\text{SiO}_2$  (neutral).

He called a *bibasic* or *sesquisilicate* a silicate in which O acid: O bases :: 3:2;  $2\text{RO}, \text{SiO}_3, 2\text{R}_2\text{O}_3, 3\text{SiO}_3$ ; O ratio; 3:2;  $9:6 = 3:2$ . Now:  $4\text{RO}, 3\text{SiO}_2 + 4\text{R}_2\text{O}_3, 9\text{SiO}_2$ ; O ratio;  $6:4 = 3:2$ ;  $18:12 = 3:2$ , and does not correspond to any of the types under  $\text{SiO}_2$  mentioned in the table I.

He called a *tribasic* or *monosilicate* a silicate in which O of acid = O of base, now called bibasic:  $3\text{RO}, \text{SiO}_3 + \text{R}_2\text{O}_3, \text{SiO}_3$ ; now:  $2\text{RO}, \text{SiO}_2 + 2\text{R}_2\text{O}_3, 3\text{SiO}_2$ .

In all that follows when the terms *acid*, *neutral*, etc., silicate are used, reference is made to silica expressed by the symbol  $\text{SiO}_2$ , and not by  $\text{SiO}_3$ , unless otherwise mentioned.

In the modern conception of the composition of the silicates, normal hydrated silicic acid has the formula  $\text{H}_4\text{SiO}_4 (=2\text{H}_2\text{O}, \text{SiO}_2)$ , a tetrabasic acid containing 4 atoms of hydrogen which can be replaced by metals. It has not been isolated, but it is probable that it exists in the pseudo-solutions coming from the dialysis of liquids containing alkaline silicates. The metasilicic hydrate is formed when solutions of dialyzed silicic hydrate are evaporated. It is probable that metasilicic acid can be condensed in the same way as metaphosphoric acid to form complex molecules of polysilicic acids. There are known: orthosilicates,  $2\text{RO}, \text{SiO}_2$ , corresponding to the normal hydrates (bibasic silicates of table I); monobasic silicates,  $\text{RO}, \text{SiO}_2$  (neutral), which seems to be derived from metasilicic acid. The real molecular constitution of the polysilicates is ignored. In most of the formulæ one is satisfied to express the ratio of oxygen of silica to oxygen of bases. In the orthosilicates (bibasic) it is 1:1 in the metasilicates (neutral) 2:1; in the trisilicates (sesquiacid) 3:1, *e. g.*, or those,  $2\text{RO}, 3\text{SiO}_2$ . In basic silicates (serpentine type) 4:3 (sesquibasic). There are other basic silicates in which it is 3:2 (dysthene).\*

Although no solid hydrate of silicic acid possessing a constant composition is known, we are acquainted with a large number of silicates forming many natural mineral species. "The hypothetical acids or hydrogen salts from which they are supposed to be derived are here given." "Molecular weights have been ascertained only for the volatile organic silicates or silicic ethers, the molecular weight of the other compounds is therefore doubtful; the oxygen ratio being the best criterion to classify them; their formulæ are represented by the simplest form possible." (Roscoe & Schorlemmer's Chemistry.)

Also, from another authority. "But scarcely any of the silicates are represented by formulæ which express their derivation from the acid.  $\text{H}_4\text{SiO}_4$ ; or other hypothetical radicals. They are generally represented as combinations of metallic oxides with

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\* Frémy.

$\text{SiO}_2$ ” (Bloxam’s chemistry): It is this mode of representation that we have adopted, using the equivalents and the formula  $\text{SiO}_2$ , for silica. In this manner the slag of composition,  $6\text{Ca}_2\text{SiO}_4$ ,  $\text{Al}_4(\text{SiO}_4)_3$ , using atomic weights and derivation from hypothetical radicals, would be represented by the formula,  $12\text{CaO}$ ;  $2\text{Al}_2\text{O}_3$ ,  $9\text{SiO}_2 = 6(2\text{CaO}, \text{SiO}_2) + 2\text{Al}_2\text{O}_3$ ,  $3\text{SiO}_2$  (O of acid = O of bases), which, referring to Table I, represents what we may call a *bibasic silicate* with RO and  $\text{R}_2\text{O}_3$ , derived from the orthosilicic acid;  $\text{H}_4\text{SiO}_4 = 2\text{H}_2\text{O}_3$ ,  $\text{SiO}_2$ . A monosilicate; orthosilicate according to modern nomenclature, (Table II). O of acid = O of bases. The tribasic or *monosilicate* of Percy,  $3\text{RO}$ ,  $\text{SiO}_3 + \text{R}_2\text{O}_3$ ,  $\text{SiO}_3$  (O of acid = O of bases) (Table I).

TABLE II.

## MONOSILICATES.

1° *Metasilicic acid*:  $\text{H}_2\text{SiO}_3 = \text{H}_2\text{O}, \text{SiO}_2$ , forming monosilicates (monobasic) O ratio 2:1 corresponding to  $\text{RO}, \text{SiO}_2$  (neutral), Ex. Enstatite  $\text{Mg}, \text{SiO}_3 = \text{MgO}, \text{SiO}_2$ . Augite (Ca, Mg)  $\text{SiO}_3 = \text{O}, 2\text{SiO}_3$ —Beryl.  $\text{Al}_2(\text{SiO}_3)_3 = \text{Al}_2 \left\{ \begin{array}{l} \text{O}_3 \\ \text{Be}_2 \end{array} \right\} \text{O}_3 \quad \text{Be}_2 \left\{ \begin{array}{l} \text{O}_3 \\ \text{Al}_2 \end{array} \right\} \text{O}_3, 2\text{SiO}_3$   
O ratio 2:1.

2° *Orthosilicic acid*  $\text{H}_4\text{SiO}_4 = 2(\text{H}_2\text{O}) \text{SiO}_2$  forming bibasic monosilicates. O ratio 1:1 corresponding to  $2\text{RO}, \text{SiO}_2$  (bibasic);  $2\text{R}_2\text{O}_3, 3\text{SiO}_2$ —Ex: Olivine,  $\text{Mg}_2, \text{SiO}_4 = 2\text{MgO}, \text{SiO}_2$ ; Phenakite,  $\text{Be}_2, \text{SiO}_4 = 2\text{BeO}, \text{SiO}_2$ .

3° *Parasilicic acid*  $\text{H}_6\text{SiO}_6 = 3\text{H}_2\text{O}, \text{SiO}_2$ ; Oxygen ratio 2:3 forming monosilicates corresponding to:  $3\text{RO}, \text{SiO}_2$  (tribasic, O ratio 2:3). Ex: Chondrodite  $\text{Mg}_3, \text{SiO}_6 = 3\text{MgO}, \text{SiO}_2$ ; Andalusite,  $\text{Al}_2, \text{SiO}_6 = \text{Al}_2\text{O}_3, \text{SiO}_2$  (tribasic silicate)  $= \text{Al}_2\text{O}_3, \frac{2}{3}\text{SiO}_3, \frac{1}{3}\text{Al}_2\text{O}_3, 2\text{SiO}_3$  O ratio = 6:9 or 2:3 as before.

## DISILICATES.

$\text{H}_2\text{Si}_2\text{O}_5 = \text{H}_2\text{O}, 2\text{SiO}_2$  O ratio: 4:1 corresponding to RO, 2  $\text{SiO}_2$  (acid silicate) O ratio 4:1, Ex: Petalite

$$\begin{aligned} (\text{Na}, \text{Li})\text{Si}_2\text{O}_5 &= \begin{array}{c} \text{Na} \\ \text{Li} \end{array} \left\{ \begin{array}{l} \text{O}, 2\text{SiO}_2 \end{array} \right\} \\ &= \underbrace{3\text{RO}, 4\text{SiO}_3}_{\text{acid silicate}} + \underbrace{4\text{Al}_2\text{O}_3, 4\text{SiO}_3} \end{aligned}$$

an acid silicate in  $\text{SiO}_3$ ; O ratio 12:3 = 4:1.

$H_6Si_2O_7 = 3H_2O, 2SiO_2$ ; O ratio 4 : 3 corresponding to  $3RO, 2SiO_2$  (sesquibasic) Ex.: Serpentine,  $Mg_3Si_2O_7 = 3MgO, 2SiO_2, 9MgO, 4SiO_2$  (sesquibasic) O ratio 12 : 9 = 4 : 3.

$H_{10}Si_2O_9 = 5H_2O, 2SiO_2$ ; O ratio 4 : 5 corresponding to  $5RO, 2SiO_2$ , Ex. Euclase  $Al_2Be_2Si_2O_9 = \frac{Al_2O_3}{2BeO} \left\{ 2SiO_2 \text{ or } \frac{Al_2}{Be_2} \right\} O_2$ ,  $2SiO_2$  O ratio 4 : 5.

## TRISILICATES.

$H_4Si_3O_8 = 2(H_2O), 3SiO_2$ ; O ratio 6 : 2 = 3 : 1 corresponding to  $2RO, 3SiO_2$  (sesquiacid) Ex.: Orthoclase  $Al_2K_2(S_3O_8)_2 = (Al_2K_2)O_4, 6SiO_2$  or  $(Al_2K_2)O_8, 12SiO_2 = 2(K_2O), 3SiO_2 + 2R_2O_3, 9SiO_2$ ; O ratio 6 : 2 = 18 : 6 = 3 : 1 =  $KO, SiO_2 + Al_2O_3, 3SiO_2$  O ratio 9 : 3 = 3 : 1 (sesquiacid).

$H_{15}Si_3O_{11} = 5(H_2O), 3SiO_2$ ; O ratio 6 : 5 Ex.: Prehnite,  $Al_2Ca_2Si_3O_{11} = \frac{Al_2O_3}{2CaO} \left\{ 3SiO_2 \right\}$ ; O ratio 6 : 5.

$H_{14}Si_3O_{13} = 7(H_2O), 3SiO_2$ ; O ratio 6 : 7 Ex.: Epidote,  $Al_2Ca_4H_2(Si_3O_{13})_2$ .

This mode of representation has the great advantage of showing at once the oxygen ratio which, certainly, the formulæ:  $6Ca_2SiO_4, Al_4(SiO_4)_3$ , and especially  $Ca_{12}Al_4(SiO_4)_9$  !!! do not *clearly* indicate as compared with:  $6(2CaO, SiO_2) + 2Al_2O_3, 3SiO_2$  or even with  $12CaO, 2Al_2O_3, 9SiO_2$ .

The atomic weights of silicon, oxygen, aluminum, calcium, magnesium, iron, manganese, barium, the oxides of which are always present in variable quantities in a slag, entering into its composition wholly or in part, being *all double the equivalents* of these elements, the formulæ of silicates, considered as "combinations of metallic oxides with  $SiO_2$ ," expressed either by using the *atomic weights or the equivalents, are then, in fact, exactly the same*. The terms monobasic or neutral, bibasic, tribasic of Table I. are based on the amount of *base* 1, 2, 3 as compared to *1 of acid*; these silicates are really monosilicates, as in the more modern conception of Table II., in which, for 1 of silica,  $SiO_2$ , there may be 1, 2, 3 of base replacing 1, 2, 3 of  $H_2O$  of the hypothetical radical. The acid silicate of Table I., containing *2 of acid* for 1 of base, is, in the same manner, a "disilicate" of modern nomenclature (Table II.);

and, for the same amount of acid, 2, there may be 1, 3, 5 of base. Likewise, the sesquiacid silicate of Table I., containing 3 of acid for 2 of base, is the modern trisilicate of Table II.: and, for this quantity, 3 of  $\text{SiO}_2$ , there may be 2, 5 or 7 of base.

In the names used in Table I. the proportion of the *basic element* has been taken as a guide in giving the name to the compound; in Table II. it is the amount of the *acid element* which has given its name to the type of silicate. In both denominations the oxygen ratio remains the same as well as the proportion of silica to bases. The whole difference lies in considerations of a certain order which may satisfy the mind as implying the idea of logical derivations from hypothetical radicals, but practically there is none, as there should not be.

The ground being thus cleared of all possible confusion in the notation we have followed and shall follow, as best conforming with data furnished by books on metallurgy and best known amongst technical blast furnace managers, let us proceed with the subject proper.

Berthier and, after him, many others (Percy, Ebelmen, Caron), have designated respectively as

*Very Fusible* = Silicates melting completely to a liquid glass at the temperature of a porcelain kiln, no blast.

*Little Fusible* = Silicates melting at the temperature of fusion of wrought iron.

*Fusible* = Silicates melting at a white heat or above in a furnace having a forced blast.

*Refractory* = Silicates not fusible or melting imperfectly at a temperature above that of fusion of wrought iron.

It is not enough that a slag should melt when it reaches the zone of the tuyeres, in the blast furnace; it must not run pasty nor thicken; it must preserve a certain fluidity when it comes in contact with the air or the sides of the forepart of the crucible. The word "fusible" indicates then a limit which it is possible to reach, but beyond which it would not be safe to go except in extraordinary cases of pressure and temperature of blast. All the silicates intermediate between "very fusible" and up to "fusible," constitute really the admissible slags.

*Fusibility of Silicates* — The *silicates* of potash and soda are very fusible in almost all proportions.

*Aluminium Silicate* — This compound, the basis of all clays, is absolutely infusible at the highest temperature of a blast furnace. The silicate containing  $73\text{SiO}_2$ ,  $27\text{Al}$ , softens a little. 3% of potash or soda is enough to cause the aluminium silicate to soften considerably; such quantities are frequently met with in iron ores.

*Calcium Silicates* — Simple calcium silicates are not generally fusible; practically only *one* of them is really fusible in the blast furnace.

LIME.	SILICA.	
88.5%	11.5%	Refractory: nearly .25 RO, $3\text{SiO}_2$ or 8RO, $\text{SiO}_2$ O of acid = $\frac{2}{3}$ = $\frac{1}{4}$ O of base.....Hectobasic.
78.0	22.0	Refractory: nearly 24 RO, $6\text{SiO}_2$ or 4RO, $\text{SiO}_2$ O of acid = $\frac{2}{3}$ = $\frac{1}{4}$ O of base.....Quadribasic
70.3	29.7	Refractory: nearly 20 RO, $8\text{SiO}_2$ , 5RO, $2\text{SiO}_2$ O of acid = $\frac{1}{4}$ O of base.....(Disilicate Table II.)
64.2	35.8	Little Fusible: 18 RO, $9\text{SiO}_2$ or 2 RO, $\text{SiO}_2$ O of acid = $\frac{2}{3}$ = O of base. Bibasic (Table I.), Monosilicate Orthosilicic (Table II.)
47.2	52.8	Fusible: 14 RO, $14\text{SiO}_2$ or RO, $\text{SiO}_2$ O of acid = $\frac{2}{3}$ = 2 $\times$ O of base.....Neutral (Table I.)
37.8	62.2	Fusible: 10 RO, $8\text{SiO}_2$ or 5RO, $4\text{SiO}_2$ O of acid = $\frac{2}{3}$ O of base.....Metasilicate (Table II.)
24.4	75.6	Little fusible: 6.8RO, $20\text{SiO}_2$ or RO, $3\text{SiO}_2$ O of acid = $\frac{1}{3}$ = 6 O of base..Triacid (Trisilicates, Table II.)

And we see from these experiments of Berthier, that the more *basic* the silicate becomes the *less* fusible it is, the neutral silicates being more fusible than the bibasic, and the latter more fusible than the quadri—and hectobasic. We see also that *beyond a certain limit of acidity* the refractory properties increase.

*Magnesium Silicates.*

MAGNESIA.	SILICA.	
72.2%	27.8%	Refractory: 28.80 MgO, $7.40\text{SiO}_2$ , nearly 4 RO, $\text{SiO}_2$ ; O of acid = $\frac{2}{3}$ = $\frac{1}{4}$ O of base. Quadribasic (Table I.)
56.5	43.5	Refractory: 22.60 MgO, $11.50\text{SiO}_2$ , nearly 2RO $\text{SiO}_2$ ; O of acid = $\frac{2}{3}$ = O of base. Bibasic (Table I.)

## MAGNESIA. SILICA.

40.1	59.9	Little fusible: 16MgO, 16SiO <sub>2</sub> , nearly RO, SiO <sub>2</sub> O of acid = $\frac{2}{3}$ = 2 O of base. Neutral (Table I.)
30.0	70.0	Little fusible: 12 MgO, 18SiO <sub>2</sub> , nearly 2RO, SiO <sub>2</sub> ; O of acid = $\frac{4}{3}$ = 4 O base. Sequibasic (Table I.)

And again, though none are "fusible" the *less* basic the silicate the *less* infusible it is.

*Double and Multiple Silicates.*

The compound silicates are enormously more fusible than any single silicate, not even excepting the alkaline silicates. They melt at a temperature much inferior to the average of the temperatures of fusion of the simple silicates composing them, this temperature being frequently *lower* than that corresponding to the fusion point of the *most fusible*, as in certain alloys, indicating, in a multiple silicate, a normal chemical combination. Lime, which forms with silica, alumina, and magnesia, but one refractory or practically infusible compound of which the simple silicates are absolutely refractory, furnish double silicates which fuse readily.

## LIME. MAGNESIA. SILICA.

17.3%	25.0%	57.5%	Very fusible: 5 (CaO, SiO <sub>2</sub> ) × 10 (MgO, SiO <sub>2</sub> ) Neutral Silicate; O of acid : O of bases : : 2 : 1
33.5	12.1	54.4	Very fusible : 4.84 (MgO, SiO <sub>2</sub> ) × 9.60 (RO, SiO <sub>2</sub> ) Neutral Silicate; O of acid : O of bases : : 2 : 1
25.0	30.0	45.0	Very fusible : 12 MgO, 7.50 SiO <sub>2</sub> , approximating 3RO, 2SiO <sub>2</sub> (Sesquibasic); O of acid, O of bases 4 : 3
19.8	14.0	66.2	Fusible : approximating 2RO, 3SiO <sub>2</sub> (Sesquiacid); O of acid : O of bases 3 : 1
9.3	20.3	70.4	Fusible : approximating 4RO, 7SiO <sub>2</sub> ; O of acid : O of bases 2 : 2 $\frac{3}{2}$ : 1
21.2	7.7	71.1	Fusible : nearly RO, 2SiO <sub>2</sub> (Acid); O of acid O of bases 37 : 9.15 4 : 1
20.9	15.8	73.3	Fusible : approx. 2RO, 3SiO <sub>2</sub> , . . . . 2RO, 3SiO <sub>2</sub> (Sesquiacid); O of acid : O of base 39 : 12.50 nearly 3 : 1



Moreover we see that the *Sesquibasic* silicates are less fusible than the *Neutral*, and again, when the silicate goes beyond a certain "acidity" it becomes less fusible.

LIME.	ALUMINA.	SILICA.	
26.1%	15.7%	58.2%	Very Fusible : $7.50 \text{ CaO}, 7.50 \text{ SiO}_2 + 2.50 \text{ R}_2\text{O}_3$ , $7.50 \text{ SiO}_2 = \text{RO}, \text{SiO}_2 + \text{R}_2\text{O}_3$ , $3 \text{ SiO}_2$ , (Neutral) 2 : 1.
34.0	16.0	50.0	Very fusible : $2.13 \text{ R}_2\text{O}_3$ , $6.15 \text{ SiO}_2 + 7.45 \text{ RO}$ , $7.20 \text{ SiO}_2$ , nearly $\text{RO}, \text{SiO}_2 + \text{R}_2\text{O}_3$ , $3 \text{ SiO}_2$ , (Neutral) 2 : 1.
26.0	31.3	43.7	Very fusible : $7.40 \text{ RO}$ , $3.70 \text{ SiO}_2 + 4.86 \text{ R}_2\text{O}_3$ , $7.95 \text{ SiO}_2$ , nearly $2 \text{ RO}, \text{SiO}_2 + 2 \text{ R}_2\text{O}_3$ , $3 \text{ SiO}_2$ , (Bibasic) 1 : 1.
36.8	22.0	41.0	Very fusible : approximating $2 \text{ RO}, \text{SiO}_2 + 2 \text{ R}_2\text{O}_3$ , $3 \text{ SiO}_2$ (Bibasic) 1 : 1.
47.3	14.2	38.4	Fusible : Exactly $2 \text{ RO}, \text{SiO}_2 + 2 \text{ R}_2\text{O}_3$ , $3 \text{ SiO}_2$ , (Bibasic) 1 : 1.
46.3	27.8	25.9	Fusible: $13.23 \text{ RO}$ , $3.35 \text{ SiO}_2 + 4.41 \text{ R}_2\text{O}_3$ , $3.45 \text{ SiO}_2$ , approximating $4 \text{ RO}, \text{SiO}_2 + 4 \text{ R}_2\text{O}_3$ , $3 \text{ SiO}_2$ , (Quadribasic) 1 : 2.
20.2	12.1	67.7	Fusible: $5.77 \text{ RO}$ , $8.65 \text{ SiO}_2$ approx. $6 \text{ RO}$ , $9 \text{ SiO}_2$ or $2 \text{ RO}, 3 \text{ SiO}_2 + 2 \text{ R}_2\text{O}_3$ , $9 \text{ SiO}_2$ , (Sesqui acid), $36.10 : 11.42 = 3 : 1$ .
10.5	19.0	70.5	Fusible: $5.77 \text{ RO}$ , $8.65 \text{ SiO}_2$ approx. $6 \text{ RO}$ , $9 \text{ SiO}_2$ or $2 \text{ RO}, 3 \text{ SiO}_2 + 2 \text{ R}_2\text{O}_3$ , $8 \text{ SiO}_2$ (Sesqui acid), $37.60 : 11.80 = 3 : 1$ .

And again, the *Neutral* slags and slags approximating the *bibasic* are more fusible than the exactly *basic* or *quadribasic* slags or those in which the acidity is beyond a certain limit, as the silicates are less basic the more fusible they become.

In certain cases, however, silica is not alone sufficient to saturate the oxides; according to ordinary laws, it has been observed that certain slags were *fusible*. It has been admitted that alumina in those circumstances can perform the functions of an acid. This is corroborated by the experiments of Berthier, who found that in the proportions given below some aluminates were fusible.

## ALUMINA. LIME. MAGNESIA.

19.9%	56.5%	23.6%, Little fusible : 6 CaO, 3MgO, Al <sub>2</sub> O <sub>3</sub> .
49.9	32.3	14.8 Fusible : 6CaO, 3MgO, 4Al <sub>2</sub> O <sub>3</sub> .
47.0	33.8	19.2 Fusible : 4CaO, 3MgO, 3Al <sub>2</sub> O <sub>3</sub> .

We find such compounds in nature : Spinel, MgO, Al<sub>2</sub>O<sub>3</sub> is fusible in the blast furnace, and certain slags containing only from 23 to 25% of silica and a large quantity of alumina have been run in English furnaces.

## MAGNESIA. ALUMINA. SILICA.

OX. RATIO.

29.3%	24.8%	45.9%, Very fusible: 4RO, 3SiO <sub>2</sub> + 4R <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> (Bibasic of Percy) ----- 24 : 16 3 : 2.
20.0	17.0	63.0 Very fusible : 8RO, 8.40 SiO <sub>2</sub> or approxim. RO, SiO <sub>2</sub> + R <sub>2</sub> O <sub>3</sub> 3SiO <sub>2</sub> (Neutral) ----- 33.6 : 16, or nearly 2 : 1.

Looking over these tables, the results of many experiments by Percy, Caron, Berthier, etc.,\* we find that of the compounds which SiO<sub>2</sub> can form with lime and alumina, or alumina and magnesia, or magnesia and lime, as a general rule, the *less basic they are the more fusible they become* until a certain *limit of acidity* is reached, and that amongst them, when the quantity of silica is *above 40% and not above 60%*, the compound becomes as much more fusible as the percentage of silica is above the first figure, varying between 40 and 60, beyond which last limit the silicate appears to fuse again with more difficulty.

In replacing in a double silicate any weight whatsoever of one of the bases by an equivalent weight of a third, a still more fusible compound is *invariably* obtained. The more complex the silicate, the more fusible and more fluid it becomes. If we consider that oxide of manganese, ferrous oxide and alkalis are always met with in slags in proportions which may reach 5 to 7%, that the alkalis, in very small quantities, increase considerably the fusibility of even the most refractory silicates, it can be better understood why unjudicious charges in limestone do not necessarily produce injurious ef-

\* Quoted in Vathaire *Les Haus Foarneaux*.

fects. A slag, for instance, which, if based upon a certain per cent. of alumina and lime would have been somewhat refractory and might have become the cause of serious trouble, acquires a greater *fusibility* and *fluidity* owing to the presence of manganous and ferrous oxides, alkalies and magnesia, derived from the limestone. Magnesia was for many years considered as a detrimental element, tending to produce infusibility! Had the iron master been aware of the conditions of fusibility of his slag and of the influence of the elements entering into its composition, affecting the said fusibility, he might have been able to reduce notably the charges in limestone, thus saving on first cost, on burden of furnace and on coal consumed, and gained at the same time in fluidity.

Within certain limits, the *more basic* the silicate the *less fusible* it is as a rule, meaning by basic not only the *number of bases* but also the *total quantity* of the basic element as compared with that of silica. The pig metal will also have more tendency to be gray as the slag is less fusible and to be white if the latter melts readily. The reason of this is found in the fact that the pig metal separates from the gangue which surrounds it only when the latter melts. If the gangue melts in the boshes at a comparatively low temperature the pig metal will pass to the hearth without stopping, reaching the crucible without having been exposed to the high temperature of the zone around the tuyeres and without having charged itself with carbon or silicon; carbon being more soluble in cast iron as the temperature of the latter is higher, and silicon being produced only by the contact of silica and iron carbides at high temperatures.

The same observations regarding the fusibility of the silicates as connected with the proportion of silica to bases apply to triple and multiple silicates as well as to double. Berthier has even remarked that, in the triple silicates of alumina, magnesia and lime, these compounds are much more fusible, as the ratio of the quantity of lime and magnesia to that of alumina approximates 3 : 1.

As an example of the fusibility of multiple silicates, according to their composition, many analyses of slags that the writer has had occasion to make in the course of his practice might be quoted. Three are here given :

1° Slag run with *white iron and a little mottled*; furnace, 40 ft. high; hot blast at 650° to 700° F.; pressure of blast, 3½ lbs. per square inch; ores, magnetites; temperature, comparatively low in the furnace.

SiO <sub>2</sub>	48.35	} 38.76	Silica is above 40%, nearly 50%. Bases in RO, 38.76% = nearly three times the alumina. 12.74% × 3 = 37.22%. Oxygen of silica : 25.98 : 18.49 oxygen of bases :: 24 : 18, nearly or 4 : 3. A sesquibasic silicate but a little <i>less basic</i> .
Al <sub>2</sub> O <sub>3</sub>	12.74		
MgO	10.71		
CaO	24.83		
Alkalies	1.01		
MnO	0.63		
FeO	1.58		

Exact ratio : 4.49 : 3.08. A good corroboration of the remarks of Berthier. Formula : 3RO, 2SiO<sub>2</sub> + R<sub>2</sub>O<sub>3</sub>SiO<sub>2</sub>, approximately.

2° Slag run with *gray iron No. 2*; furnace, 60 feet high; blast, 850° to 900° Fahr.; pressure, 7½ lbs. per square inch; temperature in furnace much higher; slag *less fusible*.

SiO <sub>2</sub>	= 40.45	} 49.61	Silica is about at the limit, 40%; bases RO = nearly 6 times bases R <sub>2</sub> O <sub>3</sub> . O of acid, 21.57 : O of bases, 19.80 :: 1.09 : 1 : approximating a bibasic slag. 2RO, SiO <sub>2</sub> + 2R <sub>2</sub> O <sub>3</sub> , 3SiO <sub>2</sub> O, ratio 1 : 1. The pig iron was gray No. 2. Slag <i>bibasic, less fusible</i> , according to the observation of Berthier, than the preceding.
Al <sub>2</sub> O <sub>3</sub>	= 8.90		
MgO	= 15.65		
CaO	28.80		
MnO	3.01		
FeO	1.00		
Alkalies	1.15		

3° Slag run in the same furnace with a change in the charges. Ores, magnetites and hematites containing 7 to 8% manganese oxide, fuel, coke and anthracite.

SiO <sub>2</sub>	= 32.65	} 37.20	Silica much below 40%. Bases in RO = 1½ times bases in R <sub>2</sub> O <sub>3</sub> . O of acid, 17.41 : O of bases 20.94 :: 1 : 1.20 : more basic than a bibasic silicate, 1 : 1.
Al <sub>2</sub> O <sub>3</sub>	= 23.00		
CaO	31.00		
MgO	0.00		
FeO	2.00		
MnO	4.20		

Formula of slag : 10.23RO, 4.35SiO<sub>2</sub> = 4.35 (2.35RO, SiO<sub>2</sub>) *less basic* than a tribasic slag, 3RO, SiO<sub>2</sub>, but *more basic* than a *bibasic* : 2RO, SiO<sub>2</sub>. Slag more basic than the preceding, consequently *less fusible*. Iron, Scotch gray No. 1, graphitic iron, kish cinder.

It seems, at least, to be established from the direct experiments of metallurgists, corroborated by blast furnace practice, that,

whatever may be the relation between the fusibility of slags and the grades of iron for simple, double or multiple silicates, the more *basic the type of the slag* the less fusible it is, as a rule.

In calculating a silicate, the saturation of the different bases for silica to produce the same type has to be taken in consideration. Considering only the principal constituents of a slag, lime, magnesia and alumina, it will readily be seen that to form an *acid slag* (Table I.)  $RO, 2SiO_2 + R_2O_3, 6SiO_2$  :

$$\text{Acid Slag} \left\{ \begin{array}{l} 1 \text{ Alumina will saturate } 3.495 \text{ SiO}_2. \\ 1 \text{ CaO} \quad \quad \quad \text{ " } \quad \quad \quad 3.000 \text{ " } \\ 1 \text{ MgO} \quad \quad \quad \text{ " } \quad \quad \quad 2.143 \text{ " } \end{array} \right.$$

And in the same manner it can be calculated that to form a neutral or a sesquibasic slag, the saturations will be as follows :

TABLE III.

ACID SLAG.	SEQUIACID SLAG.	NEUTRAL (MONOBASIC).
$RO, 2SiO_2 + R_2O_3, 6SiO_2$ $1 Al_2O_3$ will take.....3.495 $SiO_2$ $1MgO$ " .....3.000 " $1CaO$ " .....2.143 "	$2RO, 3SiO_2 + 2R_2O_3, 9SiO_2$ $1Al_2O_3$ will take.....2.6213 $SiO_2$ $1MgO$ " .....2.2223 " $1CaO$ " .....1.6071 "	$RO, SiO_2 + R_2O_3, 3SiO_2$ $1Al_2O_3$ will take... 1.7475 $SiO_2$ $1MgO$ " .....1.5000 " $1CaO$ " .....1.0714 "
SEQUIBASIC SLAG.	BIBASIC SLAG.	TRIBASIC SLAG.
$3RO, 2SiO_2 + R_2O_3, 2SiO_2$ $1Al_2O_3$ will take....1.165 $SiO_2$ $1MgO$ " .....1.000 " $1CaO$ " .....0.6714 "	$2RO, SiO_2 + 2R_2O_3, 3SiO_2$ $1Al_2O_3$ will take....0.6738 $SiO_2$ $1MgO$ " .....0.7500 " $1CaO$ " .....0.5378 "	$3RO, SiO_2 + R_2O_3, SiO_2$ $1Al_2O_3$ will take....0.5825 $SiO_2$ $1MgO$ " .....0.5000 " $1CaO$ " .....0.3571 "

Hence, 1 lb. of alumina, as far as saturation for silica is concerned, is equivalent, respectively, to

$$\begin{array}{cccccc} 3.495 & 2.6213 & 1.7475 & 1.165 & 0.8738 & 0.5825 \\ \hline 3.143 & 1.6071 & 1.0714 & 0.714 & 0.5378 & 0.3571 \end{array}$$

or to 1.631 lbs.  $CaO$ , *whatever may be the type of the silicate* ; and for the bases in  $R_2O_3$ , in general, in proportion to 1.631, as is the equivalent of one particular base of this formula to the equivalent of  $Al_2O_3$ . As to the bases in  $RO$ , requiring 1 equiv. of silica, for 1 equivalent of base to form a neutral silicate, *their equivalence* in lime is directly proportional to *their chemical equivalents*.

Hence we can calculate the following table, and say, *as far as saturation of base for silica is concerned and whatever be the type or the character of a silicate* :

TABLE III (A).

1 lb. $\text{Al}_2\text{O}_3$	= 1.631	CaO
1 lb. MgO	= 1.400	"
1 lb. FeO	= 0.780	"
1 lb. MnO	= 0.780	"
1 lb. KO	= 0.590	"
1 lb. NaO	= 0.900	"
1 lb. $\text{Fe}_2\text{O}_3$	= 1.125	"
1 lb. BaO	= 0.365	"

A glance at the above figures show *a priori*, and apart from the question of the beneficial effect that lime may have in a blast furnace in eliminating certain injurious elements of the ores, the inconsistency of using lime in excess as flux. It is, of all the principal fluxing bases of the rocks and ores, the most expensive as to cost, and the one of which the greatest quantity is required.

More of it is necessary than of magnesia or alumina to saturate, to a certain type, a given amount of  $\text{SiO}_2$ . The table shows why a *dolomite* is preferable to a *calcite*, each pound of magnesia contained in it being really equivalent to 1.40 lbs. lime, and, moreover, the double or triple silicate into which magnesia enters is much more fusible; and yet for years dolomitic limestones have been systematically rejected or sparingly used for fear "of inducing infusibility of the slag."

Suppose certain charges to have been so calculated that alumina, lime and magnesia were in proportion to silica within the figures given above: that is, 1 lb. of alumina for every 3.495 lbs.  $\text{SiO}_2$ , 1 lb. MgO for every 3 lbs. of  $\text{SiO}_2$ , 1 lb. CaO for every 2.143 lbs. of  $\text{SiO}_2$ , etc. (acid silicate, Table III.). We arrive then at the following composition for slags of the different types:

TABLE IV.

COMPOSITION.	Acid.	Sesquiacid.	Neutral.	Sesquibasic.	Biabasic.	Triabasic.
SiO <sub>2</sub> .....	73.45	67.36	58.04	47.95	40.85	31.52
Al <sub>2</sub> O <sub>3</sub> .....	7.00	8.56	10.98	13.71	15.58	18.04
MgO .....	8.15	10.10	12.89	15.97	18.15	21.01
CaO .....	11.40	13.97	18.08	22.37	25.41	29.42
	100.00	100.00	100.00	100.00	100.00	100.00

Or, taking slag of the neutral type, its composition, as taken from the preceding (Table III.) will be :

SiO <sub>2</sub> 58.04	} Such a slag, according to what has been seen above, and to the remarks of Berthier, ought to be a very fusible slag. First: It is a <i>neutral</i> slag, not very basic, consequently, silica is above 40 per cent., nearing the limit of 60 per cent. Bases in RO=30.97 =nearly $3 \times 10.97$ , the bases in R <sub>2</sub> O <sub>3</sub> . Its formula
MgO 12.89	
CaO 18.08	
Al <sub>2</sub> O <sub>3</sub> 10.97	
99.98	

is RO, SiO<sub>2</sub> + R<sub>2</sub>O<sub>3</sub> 3 SiO<sub>2</sub>. The iron run with it ought to be white or at least of a very light grade of gray. These deductions made, *a priori*, from its composition, from a study of the fusibility of silicates, find their verification in the actual results obtained in a blast furnace in England. This hypothetical slag is identical, as far as *type* is concerned, with one actually run in conditions indicating plainly a low temperature in the furnace, *i. e.*, a very fusible silicate. If, by proportioning properly the charges so as to obtain it, it were found to be more economical in use than those of the English slag, the two types being alike, all the probabilities would be—the conditions of running of the furnace being the same—that the same grade of iron would be obtained, but, in one case, much more economically than in the other.

Percy gives the following analysis of the slag of a charcoal furnace. Working as *white pig* with a little of *light mottled*—consequently of a slag run at a low temperature.

SiO <sub>2</sub> = 54.00	} If the formula of this slag were calculated it would be found to represent exactly, to the second decimal, a <i>typical neutral slag</i> . Its formula is: 2.02 R <sub>2</sub> O <sub>3</sub> , 5.97 SiO <sub>2</sub> + 8.60 RO, 8.50 SiO <sub>2</sub> or (R <sub>2</sub> O <sub>3</sub> , 2.96 SiO <sub>2</sub> ) 2.02 + 8.00 (1.01 RO, SiO <sub>2</sub> ) i. e., nearly as possible R <sub>2</sub> O <sub>3</sub> , 3 SiO <sub>2</sub> + RO SiO <sub>2</sub> :
MgO ... 0.57	
CaO ... 25.67	
Al <sub>2</sub> O <sub>3</sub> ... 13.04	
FeO ... 2.44	
MnO ... 2.20	

O of acid : O of bases : : 2 : 1; type neutral, and of the two slags, the typical one would have been obtained *at the least expense*, since, while containing about the same amount of alumina, 10.97 per cent against 13.04, and silica 54 against 58.04, it contains only 18 per cent of lime, as against nearly 26 per cent. in the other, or 50 per cent. less. A *dolomitic* limestone would have readily furnished the 13.04 per cent. MgO without using the *excess of pure calcite* with only 0.57 MgO which were necessary to obtain the 25.67, CaO required to make up for the deficiency of bases.

The formula gives of course, the means of comparing these two slags but for the determination of the oxygen of the compound a knowledge of the symbols and equivalents is absolutely necessary, a glance at the two analyses not furnishing sufficient indication as to the similitude in chemical type of the two compounds. We see in this case that silica is about the same: 54 and 58%, that *the total* proportion of bases is 42.00 in one case, against 43.92% in the English slag; but, in the typical slag, we find 18% of lime and nearly 13% of magnesia, while the English slag contains more lime, nearly 50% more, and *no* magnesia, and the apparent coincidence of quantity of silica and *total* quantity of basic elements cannot be taken as a criterion owing to the different saturation of the bases for SiO<sub>2</sub>. It can hardly be said that the two compounds are of *somewhat* the same nature, certainly they do not seem to be *identical* in type as they really are, nor could it be said that one had been obtained with a much greater economy than the other. No deductions can be drawn from their composition except through a study of their formulæ. Suppose that in the hypothetical slag a certain quantity of magnesia (8%) were replaced by a *proportionate quantity of lime* according to the equivalents of these two bases, which express also, in this case,



their *saturation* for  $\text{SiO}_2$ ; also that a quantity of 10% of alumina were replaced by the equivalent proportion of lime according to saturation of this latter base for  $\text{SiO}_2$ , as explained above; that is, at the rate of 1.631 lime for 1 of alumina and 1.40 lime for 1 of magnesia. It is clear that the silicate has preserved its character, its type, the *saturation of  $\text{SiO}_2$  by the bases remaining the same*, but its composition is considerably changed.

We have left 4.89% of magnesia, 0.97 alumina and 18.08 lime, and then making the calculation we have :

		Hypothetical Slag.	English Slag.
$\text{SiO}_2$ ...	58.04	$\text{SiO}_2$ 58.0	$\text{SiO}_2$ 53.01...54.00
$\text{MgO}$ ...	4.89	$\text{MgO}$ 4.89	$\text{MgO}$ 4.47... 0.57
$\text{Al}_2\text{O}_3$ ...	0.97	or $\text{Al}_2\text{O}_3$ 0.97	to per ct. $\text{Al}_2\text{O}_3$ 0.88...13.04
$8\text{MgO} = 8 \times 1.40 =$	11.20CaO	$\text{CaO}$ 45.97	$\text{CaO}$ 41.66...25.67
$10\text{Al}_2\text{O}_3 = 1.631 \times 10 =$	16.31CaO		
		109.49	100.00 ....

If we compare this composition with that of the English slag we find that the two analyses are quite different, and still they represent two silicates of the same type, likely to be found in a furnace under the same conditions of temperature and iron.

If, for the sake of illustration, we replace in the original typical slag, 8% of magnesia and 18 of lime by their equivalents in alumina for saturation of silica we have the composition :

	Hypothetical Slag.	English Slag.
$\text{SiO}_2$ 58.04	$\text{SiO}_2$ 63.16	$\text{SiO}_2$ 54.00
$\text{MgO}$ 4.89 or reducing	$\text{MgO}$ 5.32	$\text{MgO}$ 0.57
$\text{CaO}$ 0.08 to	$\text{CaO}$ 0.09	$\text{CaO}$ 25.07
$\text{Al}_2\text{O}_3$ 28.87 per ct.	$\text{Al}_2\text{O}_3$ 31.45	$\text{Al}_2\text{O}_3$ 13.05
	91.88	100.02

This is a perfectly *neutral silicate*, and certainly this composition does not correspond to that of the English slag.

Neither magnesia, lime, alumina, or silica correspond, nor does the sum of the bases, 38.86, in one case, 49.28 in the other, offer any bases for a comparison. Still they are *both exactly neutral slags* and to all purposes, judging from the type, would have the same fusibility, and would accompany the same grade of iron. This is going to extremes, of course, in order to show how far the differences may be characteristic. Hence, the *apparent composition of a slag does not afford any means of comparison in certain cases and no sure one in any cases*.

It has occurred to the writer, and he has used this method extensively in practice, that, instead of calculating the formulæ, slags could be readily compared in the following manner. Admitting that slags are regular compounds, multiple silicates of the bases in RO and  $R_2O_3$  of the same type, or even taking their empirical formula without any hypothesis or admission on this point, it is evident that, taking the saturation of the different bases for  $SiO_2$ , as given in the preceding table for the different types, if we calculate the proportional quantities of all the other earthy elements as *lime*, and then reduce the composition thus found to per. ct. we can show all slags to be composed simply of *silica and lime* in various proportions for each, as the case may be. If we compare the numbers thus obtained with the typical slags transformed in the same manner, we can ascertain at a glance not only to what type a given slag corresponds or between which types it falls, but also *how close* to a given type it comes; the percentage of its "*basivity*," so to speak, and this, whatever may be the number or the nature of the bases entering into the composition of the silicate, since what has been said above regarding MgO and CaO will apply, with equal truth, to all the bases of the class RO, and, as regards  $Al_2O_3$ , to all bases of the class  $R_2O_3$ .

Referring to Table III. and transforming *all* of the bases into their equivalent in lime, and reducing to per. ct.; or, calculating directly from the formulæ  $RO, 2SiO_2 \dots CaO, 2SiO_2$  (Table I.), we have:

TABLE V.

COMPOSITION.	Acid.	Sesquiacid.	Neutral.	Sesquibasic.	Bi-basic.	Tri-basic.	Quadri-basic.
$SiO_2$ % .....	68.19	61.65	51.72	41.66	34.88	26.30	21.13
CaO % .....	31.81	38.35	48.28	58.84	65.12	73.70	78.87
O of $SiO_2$ : O of bases	4 : 1	3 : 1	2 : 1	4 : 3	1 : 1	2 : 3	1 : 2
1CaO saturates $SiO_2$ * ..	2.143	1.6071	1.0714	0.714	0.588	0.357	0.268
1 $SiO_2$ " " CaO ..	0.466	0.622	0.932	1.400	1.858	2.829	3.782

NOTE A.—It must be noted here that if the corresponding formulæ, in which  $SiO_2$  is taken as the symbol for silica instead of  $SiO_2$ , had been transformed in the same way we should have

found exactly the same results as in Table V. or, at least, figures as near to the above as the differences in the numbers expressing the old and new equivalents of the same substance would have permitted; in fact, the hundredths only are affected, as previously remarked.

For instance, the formula  $2\text{RO}, \text{SiO}_2$  (Bibasic) corresponds to  $\text{SiO}_2$  to  $3\text{RO}, \text{SiO}_2$ ; the equivalent of lime was formerly taken as = 28.25, that of silica at 45.25. We should have had then for the silicate  $3\text{CaO}, \text{SiO}_2$ :

$3\text{CaO} = 84.75$	Reducing to per. ct.:	Lime, 65.19
$\text{SiO}_2 = 45.25$		Silica, 34.81
<hr/> 130.00		<hr/> 100.00

With the corrected equivalent, 28.00, and the new formula,  $2\text{RO}, \text{SiO}_2$ , we have found:

Lime, 65.13	} the difference being only in hundredths.
Silica, 34.87	
<hr/> 100.00	

Having a table of the equivalence in lime of the different bases as far as saturation for silica is concerned (Table III. (a)) the calculations are very simple. Using this method, let us compare the typical neutral slag with the English slag of Percy mentioned above.

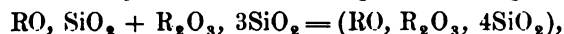
The neutral slag corresponds to  $\text{SiO}_2$  51.72%,  $\text{CaO}$  48.28 (Table V.) the English slag to and the composition of the slag is equivalent to

$\text{SiO}_2$ 54.00	or	$\text{SiO}_2$ 51.27
$\text{CaO}$ 51.33		$\text{CaO}$ 48.73
<hr/> 105.33		<hr/> 100.00
$\text{SiO}_2 = 54$ .....	54.00	} 51.33 $\text{CaO}$ .
$\text{Al}_2\text{O}_3 = .13 \times 1.631$ .....	21.25	
$\text{MgO} = 0.57 \times 1.40$ .....	0.80	
$\text{FeO} = 2.44 \times 0.78$ .....	1.90	
$\text{MnO} = 2.20 \times 0.78$ .....	1.71	
$\text{CaO} = 25.67$ .....	25.67	

Compared with the type

$\text{SiO}_2$ 51.71
$\text{CaO}$ 48.28,

the differences are as close as we can come, using two places of decimals in analyses. Both slags are neutral; O of acid : O of bases :: 2 : 1. The English slag actually run from a charcoal furnace was exactly the chemical compound having the formula



the latter being the empirical formula. The first form supposes that the silicates in,  $\text{RO}$  and  $\text{R}_2\text{O}_3$ , are of the same type, and it is difficult to conceive how it can be otherwise in a slag. A slag is a

multiple silicate having a certain fusibility quite different from that of the simple silicates which enter into its composition; it must be then that silica is *so* combined with *all* the bases as to form a compound; having a definite constitution, which can be reproduced each time that the different bases may be taken in the same proportion to each other and to the silica, each base saturating silica, according to its possible saturation in *presence of the others*, in these conditions and this presence itself modifying the type. Any change in the quantity of one of them—replacing a *given weight* of one by an *equal weight* of another—not an equivalent weight as regards saturation for  $\text{SiO}_2$ —must necessarily give rise to another saturation, since the ratio of the quantity of oxygen of the  $\text{SiO}_2$ , which has remained the same to the total amount of oxygen of the bases, which has been changed, is thereby modified.

There exists, indeed, in relation to these combinations of oxygen compounds a law by which one can readily reach the comparison of their analyses. The quantity of oxygen of one of the constituents, silica, is, in most minerals, a multiple or a sub-multiple of that of the others. The determination of these numbers furnishes ratios which can be reduced to their simplest expression. By so doing there is no hypothesis made as to the constitution of the substance, the results are furnished by the analysis itself, and if the quantity of oxygen of the acid element, silica, is divided proportionately to the quantity of oxygen found to exist in the bases in RO and to these in  $\text{R}_2\text{O}_3$ , and a rational formula deduced from the numbers thus calculated, it will be found invariably that the types of the silicates in RO and  $\text{R}_2\text{O}_3$  are the same and the same as that of the compound itself, regarded as a multiple compound in RO and  $\text{R}_2\text{O}_3$ .

When in the analysis of a mineral the ratio of the quantities of oxygen can not be simplified, it is almost always to be attributed to the fact that these minerals have rarely crystalized alone, and that in these conditions one of them may have carried with it a certain quantity of other substances, as, when several salts are found together in the same solution; these foreign substances hide, so to speak, the real proportions, modifying to some extent the characteristic properties of the mineral. Nothing of the kind at any

rate can happen with a slag, considering that its type as silicate is determined beforehand in the charges of a blast furnace, by furnishing to the silica of ores, stone, and ash of coal, perfectly definite basic elements, in certain proportions primarily calculated, which necessarily determine a composition which the ultimate analysis of the slag, as run from the furnace, corroborates very closely in the great majority of cases. When it does not happen, it has also to be attributed to disturbing factors, and they can be found, for instance, in this fact that calcium, combined with sulphur, which the slags often contain in very serious quantities, has been calculated as oxide of calcium or *lime*. The same can be said of magnesium and manganese. 5% of sulphur in a slag is by no means an exceptional circumstance; 8% of manganese sulphide is frequently met with in Scotch slags. In other cases alumina, owing to certain condition of the furnace, or the proportions of fluxes, will play the part of an acid, and, in these conditions, ought not to figure in the determinations of the type as saturating silica.

(To be continued.)

#### DETERMINATION OF LITHIA IN MINERAL WATERS.

By E. WALLER, PH. D.

Practically, three methods are now available. 1. The phosphate method (Mayer's modification) (*Ann. Chem. u. Pharm.* **98**, 193). 2. The amylalcohol method (*Gooch, Am. Chem. Jour.*, **9**, 33). 3. The fluoride method (*Carnot, Bull. Soc. Chim.* [3] **1**, 280).

Rammelsberg's method (*Pogg. Ann.*, **66**, 79) somewhat similar in principle to that of Gooch, in that it depends upon the comparatively greater solubility of lithium chloride in an organic solvent, has been comparatively little used, on account of the difficulty and expense involved in obtaining the pure anhydrous alcohol and ether necessary for the process. Moreover the experiments of J. L. Smith (*Am. Jour. Sci.* [2] **16**, 56), rearranged in convenient form for reference by Gooch (*loc. cit.*) do not indicate that it is

very satisfactory in its application, even with the best of care. Some indirect processes, such as the weighing of mixed chlorides of sodium, potassium and lithium, and then determining the chlorine and potassium (Bunsen, *Ann. Chem. u. Pharm.*, 122, 348), have been also proposed, but they are troublesome in execution, and likely to be unsatisfactory in result.

For all of these processes, it is necessary to obtain from some known quantity of the water, the alkalies as chlorides free from admixture with other bases, and in most cases, a considerable proportion of the sodium and potassium salts, which usually predominate largely over those of lithium, must be removed. To accomplish this the usual method may be followed, acidification with hydrochloric acid, evaporation, treatment with barium hydrate solution, removal of the excess of baryta by ammonium carbonate, driving off the ammonium salts, and extraction with alcohol or alcohol and ether, to take out the lithium chloride which is inevitably accompanied by some sodium and potassium chlorides. Throughout this treatment, the spectroscope must constantly be used to determine when the extraction or washing is complete and these preliminary operations often prove very tedious. Some suggestions in this connection may be of value. The small platinum wires used to test the precipitates, solutions, etc., need critical examination. A wire which has been once used with lithium salts may perhaps be held in the flame until it will give no trace of color to the flame, nor show the lithium line by the spectroscope, but on moistening with hydrochloric acid and inserting in the flame, the line will show almost as brightly and distinctly as if no lithium had been removed from it. Repeated scouring, immersion in acid and insertion in the flame, or long soaking in acid may be necessary to remove this trace of lithium from the wires. It has been found convenient to keep several wires dipping into a test tube partially filled with dilute hydrochloric acid, and to use them in succession, so that each wire shall have a tolerably long immersion in the acid, before being tested again, as a preliminary to using it for a test on a precipitate, etc.

Barium precipitates ( $\text{Ba CO}_3$  and  $\text{Ba SO}_4$ ) when formed in the presence of lithium compounds, carry down and retain perceptible

quantities of lithia (by spectroscopic test) with great persistency. The well known tendency of the barium sulphate to drag other salts with it *seems* to be greater in the case of lithia than in that of other alkaline salts, although this may perhaps be due to the exceeding delicacy of the spectroscopic reaction. Precipitation in a rather dilute solution, and rather liberal washing is usually the most convenient course to pursue in the case of the precipitation of  $\text{Ba SO}_4$  in presence of lithium salts. With  $\text{Ba CO}_3$ , re-solution in  $\text{HCl}$ , and re-precipitation with ammonia and ammonium carbonate is most effective. If the proportion of lithium is large, re-solution, and re-precipitation a third time, may be advisable. The precipitate produced by barium hydrate, unless consisting largely of sulphate, does not give so much difficulty in the washing out of the lithia, except when it has been exposed for some time to the air of the laboratory containing  $\text{CO}_2$ .

A word further as to the decomposition of  $\text{Li Cl}$  by heat. Direct quantitative estimations upon the subject were not made in this investigation, but the phenomena noted tend to confirm Mayer's remark that under the influence of heat in presence of water, lithium chloride has a tendency to exchange chlorine for oxygen.

A solution containing lithium chloride is evaporated to dryness with difficulty when placed on the water bath, and if it finally is made to *appear* dry after prolonged treatment in this manner, more of the material is slow to re-dissolve in water (apparently because of the formation of lithium hydrate) than if the same solution is evaporated nearly to dryness and the moisture driven out by careful ignition over a naked flame.

Assuming in every case that one has obtained a concentrated aqueous solution from a known quantity of the water, containing all of the lithium and some of the potassium and sodium as chlorides, but no other bases, the phosphate method would be as follows :

Add an excess of hydro-disodium phosphate, and then a moderate excess of pure sodium hydrate, evaporate to dryness, re-dissolve in water by the aid of a gentle heat, add an equal volume of strong ammonia, digest warm for some time, allow to stand for twelve hours, filter and wash with a mixture of equal volumes of ammonia

and water, and finally ignite and weigh as  $\text{Li}_3\text{PO}_4$ . A second or third portion of precipitate may be recovered, by evaporating the filtrate and washings, adding ammonia and allowing to stand as before, filtering, etc. The chief difficulty with the accuracy of the process, consists in the practical impossibility of obtaining all the lithium as phosphate, free from any other alkaline salts. Too much washing will cause appreciable amounts of lithium phosphate to go into solution. Indeed, in my experience the filtrate and washings have always showed a decided lithia line in the spectro-scope, from the start. On the other hand, too little washing leaves some alkaline salt along with the lithium phosphate—shown by its tendency to cake on ignition—but whether it cakes or not, lithium phosphate separated by this method when tested by the flame, almost invariably gives so strong a sodium flame, as practically to obscure the red of the lithium to the naked eye. Consequently it becomes to a considerable extent a matter of judgment, to decide when the washing is completed, and *then* the amount of lithium phosphate obtained is a compromise between the precipitate dissolved off by washing, and alkaline salts left with it. However, by the aid of a little experience, the error can be usually brought within moderate limits, if the proportion of water which the chlorides represent is sufficiently large (ordinarily 10 to 20 litres). The use of such large quantities of water is naturally attended with more or less labor, in evaporation, removal of bases, etc., and is in itself objectionable aside from the sources of error inherent in the method of determination. This method has, however, until recently been practically the only one in general use.

The method of Gooch (*loc. cit.*) used by him in the examination of the waters of the Yellowstone Park (*Bull. U. S. Geol. Survey*, No. 47, also *Chem. News*, 59, 113, *et seq.*), may be described as follows: The concentrated solution of the alkaline chlorides should contain only about 0.2 grm. of salts in all. To this solution, in a casserole or dish, is added 30 to 50 c. c. of pure *anhydrous* amyl alcohol. The vessel is then heated on a sand bath over a low flame, so as to boil off the water through the amyl alcohol, leaving the undissolved salts adhering to the sides of the dish. The heat is kept up until the volume of amyl alcohol has



been reduced to about 15 or 18 c. c. after cooling. A few drops of hydrochloric acid are added to restore to the form of chloride any lithium oxide or hydrate which may have been formed, and the heating is repeated for a short time. The amyl alcohol is then filtered through paper, or through a Gooch crucible, into a measuring cylinder, and its volume noted (usually 10 to 15 c. c.). In case the proportion of lithium is large the undissolved salts should be taken up with a little water, and the treatment repeated in the same way as just described, the amount of amyl alcohol which has been heated with the chlorides being measured as before. The salts are then washed with cold amyl alcohol until no trace of lithium is perceptible in them by the spectroscope; the filtrate and washings are evaporated in a weighed platinum dish, and the chlorides converted into sulphates, ignited and weighed. From this weight, for every 10 c. c. of amyl alcohol which remained in contact with the chlorides after heating, the following deduction is made:

When only sodium and lithium chlorides were present, 0.00050 gm.

“ “ potassium “ “ “ “ 0.00059 “

When both sodium and potassium, as well as lithium

chlorides were present, - - - 0.00109 “

The cold amyl alcohol used for washing dissolves so little that it is needless to take it into account.

The relative solubilities of Na Cl, KCl and Li Cl in amyl alcohol, as determined by Gooch, are essentially:

Na Cl.....	1 in 30,000, or 0.0041 gm. in 100 c. c.
K Cl.....	1 “ 24,000, or 0.0051 “ 100 “
Li Cl.....	1 “ 15, or 6.60 “ 100 “

Temperature seems to have but little influence upon the solubility of Na Cl and KCl.

Pure amyl alcohol freed from water by boiling, if necessary, is indispensable.

Gooch's test experiments with mixtures of pure salts may be here quoted, arranged in a form slightly different from that given in his paper. The  $\text{Li}_2\text{SO}_4$  obtained was calculated back to Li Cl in every case. The error is noticeably greater in the presence of potassium chloride.

Ex. pt. No.	Conditions.	Li Cl taken.	Errors in corrected weight of Li Cl found.
(23)	Na Cl only } Single	0.1298 grm.	0.0002— grm.
(24)	" " { Extr'n	0.1227 "	0.0002— "
(32)	" " { Double	0.1287 "	0.0007— "
(33)	" " { Extr'n	0.1347 "	0.0006+ "
(26)	KCl only } Single	0.1256 "	0.0008— "
(27)	" " { Extr'n	0.1287 "	0.0010— "
(34)	" " { Double	0.1125 "	0.0003+ "
(35)	" " { Extr'n	0.1251 "	0.00011+ "

The average of these errors is 0.0001— with a range from 0.001— to 0.0011+ or if we calculate to the equivalent in Li H CO<sub>3</sub> from 0.0016— to 0.00176+, a difference of 0.00376 grm.

The process has the advantage that the sodium and potassium chlorides are left in a condition for the determination of those bases, in which case, however, an allowance must be made for the small amounts dissolved by the amyl alcohol which was heated with the chlorides. One disadvantage of the process is to be found in the fumes of the amyl alcohol which, even in a well ventilated laboratory is a source of great discomfort to most analysts.

The small amount of water, 100 to 200 c. c. that can be used for this process is advantageous, though for those accustomed to the use of the phosphate process, the amount seems hardly large enough to give a fair average, and to average on a larger amount requires the concentration of the Li Cl by extraction with alcohol or alcohol and ether. In some of the first trials made with the process, the amount of mixed chlorides experimented upon considerably exceeded 0.2 grm., probably nearly 1. grm. and in some cases more. This was because Prof. Gooch's paper seemed to imply that the operation might be reasonably expected to be successful, when applied to quantities ordinarily handled in analytical work. In the case of one water it did prove so, but with another water, containing more lithia as well as alkaline salts it was not. The removal of all the water in the manner described, was a matter of extreme difficulty, and curiously enough, a limit seemed to be reached, beyond which the Li Cl was extracted, but slowly and with great difficulty. The results may prove interesting.

The alkaline salts from two equal quantities of a water, each lot amounting to between one and two grammes, were treated as described :

Obtained from A.....	0.2400	grm. $\text{Li}_2\text{SO}_4$ from B	0.2354	$\text{Li}_2\text{SO}_4$
Found in insoluble part. f. A.....	0.0974	“ “ B	0.0943	“
Total.....	0.3374	“ “	0.3297	“

The control process used in this case was Carnot's fluoride method, which cannot however be regarded as absolutely free from imperfections. It is as follows: the mixed alkaline chlorides after evaporation nearly to dryness, are extracted with a mixture of about equal volumes of alcohol (of 90% or over) and ether, so as to obtain the  $\text{Li Cl}$  comparatively free from the others. It was found most convenient to add the alcohol ether mixture, and allow to stand for some time with frequent stirring, and then after standing over night to filter through a small filter, and wash with alcohol, one extraction will often suffice. A second extraction may however be necessary, the work being of course controlled by the indications of the spectroscope. After evaporating off the alcohol and ether, the salts are dissolved in the least possible quantity of water, and filtered into a weighed platinum dish. The filtrate and washings should then be concentrated to small bulk (5 or 10 c.c.) and pure ammonium fluoride and ammonia added; after thorough mixing the dish is set aside over night for the  $\text{Li F}$  to precipitate. The solution is then decanted through a small filter, and the precipitate is washed by decantation three or four times (5 to 7 c.c. at a time), with a solution consisting of the reagent mixed with 5 to 10 times its bulk of ammonia; between decantations the solution must be allowed to stand some little time with stirring. The bulk of filtrate and washing (30 to 50 c.c.) is noted, the filter paper and contents placed in the dish, sulphuric acid added, and heat applied until the paper has been incinerated, and the lithium converted to sulphate, in which form it is weighed. To this weight is added 0.0040 grm. for every 7 c.c. of filtrate and washings, and the result estimated as  $\text{Li}_2\text{SO}_4$  is calculated to  $\text{Li}$ ,  $\text{Li HCO}_3$ , etc., according to the requirements of the case.

Care is necessary in preparing the reagent, and wash liquor.

Carnot seems to have found that the ammonium fluoride ordinarily supplied for laboratory use, is the only member of the combination liable to contain impurities which would interfere (chiefly fluosilicic acid, which might precipitate alkaline fluosilicates), but

experiments have shown that ammonia, which has been standing for some time in contact with glass, will give a cloud (presumably ammonium fluosilicate) with a mixture of solutions of ammonium fluoride and ammonia after boiling and filtering clear. This solution, so long as it contains a fair amount of free ammonia, appears to be without action upon glass. It has been found advisable therefore to make up (and cork up) the reagent and washing solution some time beforehand, and to filter off such portions as may be required at the time of using. Naturally, it is necessary to use for the final filtration, a filter paper which has been extracted with hydrofluoric acid. Schleicher & Schull's papers were found satisfactory in this connection. Carnot also recommends that the resulting  $\text{Li}_2\text{SO}_4$  should be dissolved in 40 to 50 c.c. of water, and a test made for the presence of magnesium, which may have remained with the alkaline chlorides. If any is found to be present, it must be determined as phosphate and a correction made accordingly.

In connection with this process it was observed that lithium sulphate ignited in contact with the carbon of the filter paper, is especially prone to reduce to sulphide and especial caution is necessary at this stage of the operation. The sulphide, when heated in contact with the platinum, attacks it in a very marked manner.

The process seems to be very good, although not rapid.

Its tendency is to yield results a little high, apparently because the allowance for solubility is usually larger than the actual amounts of precipitate dissolved. Test analysis tended to show also that unless the amounts of potassium and sodium chlorides present with the lithia are kept within narrow limits, the results will be high.

Unfortunately a number of the tests and comparison experiments with these methods have not yet been completed, and will have to be deferred to a second communication.

In order to test these methods upon water containing lithia, samples of several of the best known and widely advertised waters were purchased and submitted to examination.

The results were somewhat surprising, and showed unquestionably that either the original analyses, on the strength of which those waters are now sold, were erroneous, on account of imper-

fection in the methods used, or, what is more probable, that the proportions of lithium in those waters are liable to great fluctuations.

The results given were chiefly obtained by Carnot's fluoride method, but were in several cases confirmed by the use of other methods. The most scrupulous care was exercised to be sure of obtaining *all* of the lithium in the waters under examination, the spectroscopic indications having been used at every stage of the process.

In the Farmville Lithia Water, purchased at the office of the company, no lithium could be detected by the spectroscope on moderate amounts of the water. On evaporating eight litres of the water, and treating in the manner described for the concentration of the lithia into a solution of small bulk, a lithia line was obtained in the spectroscope, but the amount was found to be too small to permit of a quantitative estimation. The experiment was repeated with ten litres of the water, with essentially the same result.

With the Buffalo Lithia Water the reaction for lithium was more distinct, when considerable quantities of the water were concentrated. From 20 litres of the water was obtained lithium sulphate corresponding to 0.0185 part  $\text{Li HCO}_3$  per 100,000.

In the Londonderry water, the lithia reaction could be obtained without great difficulty. Analysis of the water purchased by myself showed a little over 4 parts per 100,000. The company puts up some of the water in half-gallon bottles not charged with  $\text{CO}_2$ , and also some in pint bottles (called in their circulars "sulpho-carbonated"), which is charged with  $\text{CO}_2$ , and has also received the addition of some salts. The amounts of salts added appears to be somewhat irregular. For instance, the following results were obtained (results given in parts per 100,000) :

	Total solids.	Loss on ign.
Londonderry, half-gallon bottles (aver.).....	37.35	2.25
"      pint bottle, A.....	149.4	4.9
"      "      B.....	104.2	4.5
Average of eleven others.....	224.7	6.4

The variations in the eleven bottles were 221.3 to 231.4, for total solids. The proportion of lithium was essentially the same as for the still water.

I was told that several lots of water, purporting to come from these springs, had at times appeared on the market in which no lithia could be detected. As I learned that Dr. Endemann had obtained some water of that kind, I requested him to send me a bottle. He complied, and although the bottle bore all the labels and marks similar to those purchased by myself, no lithia could be detected in it. The water contained 5.2 parts total solids per 100,000. I have heard of others who had similar experiences.

I naturally desired to obtain samples of these waters direct from the springs, taken by some one whom I knew to be disinterested. Attempts thus far have been unsuccessful. In the case of the Londonderry springs, all access is denied to visitors, and applications for water are referred to the bottling establishment in Nashua.

Of all the waters examined, purporting to be natural, the Saratoga Hathorn proved to be the strongest in lithia. The result of tests on this water are not at present in such form that they can be here recorded, but it suffices to say that the water contains fully as much as the analyses call for (12 to 14 parts  $\text{Li HCO}_3$  per 100,000, corresponding to 7 or 8 grains per U. S. gallon).

Tests were also made on the waters manufactured and sold by Carl H. Schultz as containing lithia. They were found to contain a little more lithia than claimed. E. g., the formula on his "Vichy with Lithia," calls for an amount corresponding to about 57 parts  $\text{Li HCO}_3$  per 100,000. The analyses showed 60 to 62 parts.

The results enumerated may be thus tabulated :

Designation of Water, etc.	Total Sds. Per 100,000.	Loss on Ign.	Non-Volatile.	$\text{Li HCO}_3$		
				Used for Determination.	Per 100,000	Gr. U. S. Gal. Gr. Imp. Gal.
Farmville Lithia, half gal. bottles	16.4	1.1	15.3	8. L	traces.	
" " " " " "	"	"	"	10. L	traces.	
Buffalo Lithia, half gal. bottles...	93.2	6.5	88.7	20. L	0.0185	0.011 0.013
" " " " " "	"	"	"	20. L	0.0135	0.008 0.009
Londonderry Lithia hf. gal. bot's.	37.35	2.25	35.1	10. L	4.171	2.432 2.920
" " " " " "	"	"	"	10. L	4.075	2.376 2.852
" " " " " "	"	"	"	2. L	4.130	2.408 2.891
" " pts (c'h'g'd $\text{CO}_2$ )	"	"	"	2. L	4.129	2.407 2.890
" " " " " "	"	"	"	4. L	4.074	2.376 2.851
" " (hf. gal. Dr. E.)	5.1	1.	4.1	1. L	none	

## ABSTRACTS.

### GENERAL AND INORGANIC CHEMISTRY.

#### **Eukairite from Argentina.** ROBERT OTTO.

Berzelius and later A. E. Nordenskjöld analyzed a rare mineral, consisting of an equal number of atoms of silver, copper and selenium. This mineral was found in minute quantities in the copper mine Skrikerum in Smöland, Sweden. Emil Hünicken has found in Villa Argentina, Prov. Rioja, Argentine Republic, in Arnango in the Andes of Famatina and in other places, a peculiar mineral, which was sent for exact analysis to the author. The mineral occurs in veins, some of which have a width of 1 c.m. but at a depth of 14 m. are 35 c.m. broad. The mineral, according to analysis, is the same as Berzelius' Eukairite, and consists of :

Ag = 42, 7 per cent.

Cu = 25, 5      "

Se = 31, 5      "

(*Ber. d. Chem. Ges.*, **23**, 1039.)

L. H. F.

#### **On Spontaneously Inflammable Hydrogen phosphide.** L. GATTERMANN and W. HAUSKNECHT.

For the extensive and interesting details of this remarkable research we refer to the original paper. This liquid phosphine was obtained pure from calcium phosphide prepared in an original manner. An analytical determination of phosphorus was not feasible. But the hydrogen was determined by means of combustion with lead chromate. Figures were found agreeing with the formula  $\text{PH}_2$ . Also the decomposition by sunlight furnishes figures corresponding to that formula. The attempt to determine the vapor density in V. Meyer's apparatus, below the boiling point of the substance, using methyl iodide as a mantle, was not successful. Quite a number of determinations pointed towards the formula  $\text{P}_2\text{H}_4$  (66) since values such as : 74, 73 and 77 were obtained.

The boiling point was determined successfully. It does *not* lie at temperatures between 30° and 40° C., as the handbooks state,

but was found to be 57° to 58° C., at 735 m. m. The following figures were found in determining the specific gravity :

(I.) Spec. Grav., 1.016.

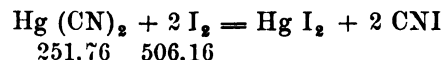
(II.) Spec. Grav., 1.007.

It follows that this hydrogen phosphide is slightly heavier than water, and this fact was confirmed by direct experiment which showed a large drop of the liquid to sink in water. (*Ber. d. Chem. Ges.*, 23, 1174, 1890.) L. H. F.

#### Vapor Density and Melting Point of Cyanogen Iodide.

KARL SEUBERT and WILLIAM POLLARD.

The two above named determinations have heretofore not been performed. The substance is very volatile and strongly poisonous. The cyanogen iodide was prepared in the manner used by Davy and described by Serullas; action of iodine upon mercuric cyanide. The equation :



calls for one part of mercuric cyanide and two parts of iodine, while Serullas recommends exactly the reverse, *i. e.*, 2 pts. Hg (CN)<sub>2</sub> to 1 pt. of iodine. The great excess of the former should prevent volatilization of free iodine. The authors used mixtures according to the above equation or in the proportion of equal parts of the two substances. But they were careful to allow the reaction to take place very slowly and spontaneously, in direct sunlight, during 2 to 3 days, using peculiar apparatus. The product obtained, which cannot easily be analyzed gravimetrically, allowed titration in the simple manner, given by E. v. Meyer. According to the latter, cyanogen iodide and hydriodic acid, *in excess*, decompose as follows :



The liberated iodine is titrated in the ordinary manner. Instead of using a solution of HI, E. v. Meyer proposes to apply a solution of KI acidulated with H<sub>2</sub>SO<sub>4</sub>. The vapor density obtained by Victor Meyer's method led to the formula CNI, analogous to CNCl and CNBr. The melting point was determined in the ordinary way, in a capillary tube, but this latter had to be sealed



at both ends, the substance volatilizing below its melting point. The bath used was  $\text{H}_2\text{SO}_4$ . The results obtained were :

	<u>Melting Point.</u>	<u>Congeaing Point.</u>
a.....	146,5°	143°
b.....	146,5°	142,5°
c.....	146,5°	142,5°

(*Ber. d. Chem. Ges.*, **23**, 1062.)

L. II. F.

### A New Apparatus for Determination of Melting Point.

A. C. CHRISTOMANOS.

This interesting apparatus allows the substance, the melting point of which is to be determined, to float on mercury, which can be heated, while a little mercury rests on top of the substance. An electric bell is connected with the two quantities of mercury, separated from one another by the substance to be tested. When the latter melts, the mercury flows together, the bell rings and the thermometer is read. (*Ber. d. Chem. Ges.*, **23**, 1093.) L. II. F.

## ORGANIC CHEMISTRY.

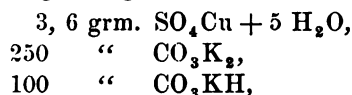
### Determination of Different Sugars by Cupro-potassium Carbonate Solution. H. Ost.

This research is based upon the proposition which was made in 1876 by A. Soldaini, to use a solution of copper carbonate in potassium bicarbonate instead of Fehling's solution. This solution has, so far, not been adopted because it is difficult to obtain of constant composition and because its action upon invert sugar is too slow. The author proposes two solutions, which have been useful to him. One consists of :

23, 5 grms. cryst. copper sulphate,  
 250    "   potassium carbonate,  
 100    "   potassium bicarbonate,

per litre. First the potassium salts are dissolved, then the copper solution is gradually added. The action of this solution depends not only upon the presence of copper, but also upon that of potassium carbonates and upon the strength of the sugar solution. It

is available for volumetric as well as gravimetric analysis, and is applicable for titrations of mixtures of sucrose with but little glucose. Fehling's reagent gives very unreliable results for such mixtures. Besides this, the end of the reaction, which is manifested by a yellow coloration when using Fehling's solution, is indicated for the above liquid by a colorless, transparent appearance of the mixture. For sucrose very poor in glucose, as for instance in beet sugar, the above solution is too concentrated, and a solution of the following strength is used :

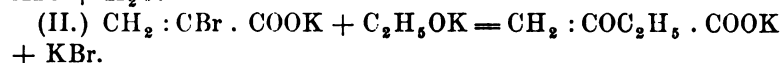
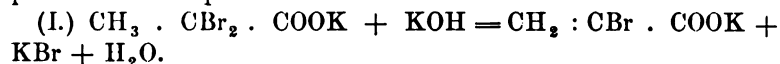


per litre. This solution should only be used gravimetrically. (*Ber. d. Chem. Ges.*, **23**, 1035.) L. H. F.

#### Ethoxyacrylic Acid from $\alpha$ -Dichloropropionic Acid.

ROBERT OTTO.

According to W. Merz alcoholic potassium, when acting upon  $\alpha$ -dibromopropionic acid forms ethoxyacrylic acid. The reaction performs in two phases :



The author, together with G. Holst has now prepared this same acid from  $\alpha$ -dichloropropionic acid. It forms white crystals, melting at  $110^\circ \text{C}$ . (*Ber. d. Chem. Ges.*, **23**, 1108, 1890.) L. H. F.

#### Friedel-Craft's Synthesis of Ketones from Phenolethers.

L. GATTERMANN, R. EHRHARDT and H. MAISCH.

The results obtained are summed up by the authors as follows :

Phenolethers react very smoothly with acid chlorides, forming ketones of extraordinary capacity of crystallization. Almost all of them may be obtained in measurable crystals. Mineralogists are thus offered splendid material to study the relations between form of crystals and constitution. The law which Leuckart noticed for phenyl cyanate and which Gattermann observed for urea chloride

with hydrocarbons and phenolethers, is illustrated, namely, that, in the case of an unoccupied para position, this is filled out by the acid residue entering. Sometimes, besides the normal ketone, an unsaturated alkylene compound is formed. This latter is generated from one molecule of a normal ketone and one molecule of un-attacked phenolether by the joint loss of water. (*Ber. d. Chem. Ges.*, 23, 1199, 1890).

L. H. F.

**Action of Ammonia on Di- and Tri- Halogenated Substitution Products of Hydrocarbons.** P. GALEWSKY.

It has been shown of late by Udransky and Baumann that diamines may be precipitated almost quantitatively from very dilute, aqueous solutions by treating these with benzoyl chloride and dilute NaOH. The precipitates represent the corresponding benzoyl compounds. The present research was commenced with the intention to learn by means of this benzoylchloride reaction, whether alkylene bromides, treated with alcoholic ammonia in the cold, would yield diamines even in small quantity. Ethylene bromide allowed the formation of the diamine at ordinary temperature, propylene bromide required higher temperature. Tribromallyl yielded neither a di- nor a tri- amine, but as a result of this reaction a brominated monamine was formed:



The amine was proved to be identical with the bromallylamine recently prepared by Paal and Herman; it may have either of the following constitutional formulæ:

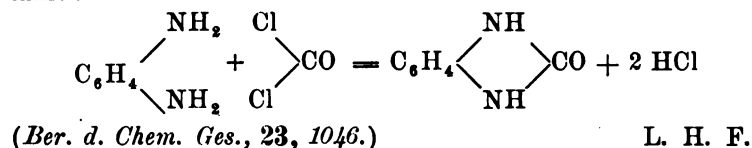


It should be remarked, that the bromine atom is very closely linked in this compound and does not admit of the formation of a diamine when heated with alcoholic ammonia to 200° C. The yield of bromallylamine according to the above method is not at all a quantitative one. (*Ber. d. Chem. Ges.*, 23, 1066.) L. H. F.

**Action of Phosgen upon o-Diamines.** A. HARTMANN.

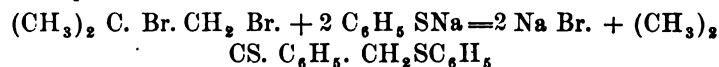
Heretofore this action has only been mentioned by Michler and Zimmermann in regard to m-phenyldiamine. It has now been

studied further and it is found that a ring-formed, closed chain of ureas is obtained under the influence of phosgen, which occurs in general according to the following equation for phenylendiamine :

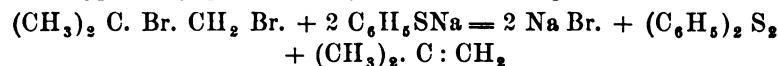


**Behavior of Sodiumphenyl mercaptide with Isobutylenbromide.** ROBERT OTTO.

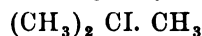
This reaction did not take place in a normal manner, according to the equation :



but, apparently quantitatively, in the following manner :



yielding sodium bromide, phenylene disulphide and *isobutylene*. This latter, under the influence of hydriodic acid, was easily transformed into the iodide of tertiary butylic alcohol :



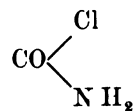
boiling at 98° to 99° C.

(*Ber. d. Chem. Ges.*, 23, 1051.)

L. H. F.

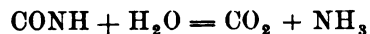
**A Modification of the Urea chloride Synthesis.** L. GATTERMANN and A. ROSSOLYMO.

About two years ago a method was described by Gattermann, Schmidt, Hess and Harris, according to which



reacting with aromatic hydrocarbons and phenoleters in the presence of aluminium chloride effects a synthesis of carbo acids. Urea chloride is formed from phosgene and ammonium chloride.

Large quantities of liquefied phosgene gas are necessary for this reaction. In order to simplify the method, it was attempted to avoid the use of phosgene. Since urea chloride at the higher temperatures at which these syntheses were performed dissociates into cyanic acid and hydrochloric acid, the use of a mixture of these two was indicated. Cyanic acid may be prepared from cyanuric acid, which furnishes three molecules of the former, when heated carefully. It should be remarked, that although it was found that the mixture of cyanic acid and hydrochloric acid allowed a synthesis in the above mentioned sense for *small* quantities of carboxylic acids, the old method, using urea chloride has to be resorted to when larger quantities are desired. Cyanuric acid was prepared by the action of bromine upon potassium ferricyanide. It has to be applied in a perfectly anhydrous state, because *cyanic* acid, when brought in contact with water decomposes, according to the equation.



The following table shows the hydrocarbons or phenoleters used in this manner and the melting points of the acid amides obtained :

Hydrocarbons or Phenoleters.	Melting Point of the Acid Amide.
Benzol.....	127° C
Toluol.....	156 "
o-Xylol.....	165 "
m-Xylol.....	180 "
p-Xylol.....	186 "
Pseudocumol.....	200 "
Durol.....	173 "
Naphthalene.....	202 "
Acenaphthene.....	198 "
Anisol.....	163 "
Phenetol.....	202 "
$\alpha$ -Naphthylmethylether.....	234 "
$\alpha$ -Naphthylethylether.....	244 "
$\beta$ -Naphthylmethylether.....	186 "
$\beta$ -Naphthylethylether.....	161 "

(Ber. d. Chem. Ges., 23, 1190, 1890.)

L. H. F.

**Aldehydes of the Hydrocynnamic Acid Series.** W. VON MILLER and G. ROHDE.

According to the preceding communication, the data found in the literature of hydrocynnamic aldehydes are to be stricken out. The authors have now prepared some genuine representatives of this series, which offer, besides the other well known characteristics of *aldehydes*, the following special ones :

1. They possess a very characteristic and agreeable odor, suggestive of lilac or jessamine ;
2. With concentrated or slightly diluted sulphuric acid they furnish liquids which, in transmitted light, are more or less intensely rose or carmine colored.

These aldehydes were prepared by means of destructive distillation of the calcium salts of the corresponding acids with calcium formate. (*Ber. d. Chem. Ges.*, **23**, 1079.) L. H. F.

**On Sulphocyanogen and Selenocyanogen Compounds.** L. HAGELBERG.

Buff and Sonnenschein discovered ethylene rhodanide almost simultaneously in the year 1855. In 1874, Lermontoff prepared the methylene rhodanide. No other dirhodanides of the formula  $C_n H_{2n} (SCN)_2$  are known in the fatty series. The author has now prepared :

Trimethylene rhodanide= $NCS. CH_2. CH_2. CH_2. SCN$

Propylene rhodanide= $CH_3. CH. SCN. CH_2. SCN$

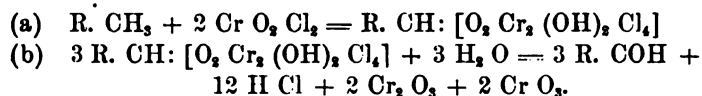
Propylene selenocyanide= $CH_3. CH. Se. CN. CH_2. Se CN$

and derivatives of these compounds. (*Ber. d. Chem. Ges.*, **23**, 1083.) L. H. F.

**Contributions to a Knowledge of Etard's Reaction.** W. VON MILLER and G. ROHDE.

The authors intended to perform the synthesis of indene derivatives starting from cynnamic aldehydes. This synthesis would have implied the assumption of a formation of hydrocinnamic aldehydes. According to Etard, hydrocynnamic aldehyde can be prepared from propylbenzol by the action of chromyl chloride. He maintained that, as with the other homologues of benzol, the re-

action was accomplished according to the following two equations:



The authors, in treating propylbenzol in this way did *not* obtain hydrocinnamic aldehyde but its isomere, benzylmethylketone together with benzaldehyde. When the mixture of these two latter was treated with oxidizing reagents, stilbene resulted. Hydrocinnamic aldehyde alone, or mixed with benzaldehyde, when subjected to a condensation experiment does *not* furnish stilbene.

Thus Etard's reaction, which formerly was considered as one leading to aldehydes, had in this case generated a ketone. A series of critical experiments, performed with cymol and ethylbenzol in the same manner, showed that also in these cases ketones are formed, contrary to Etard's data; phenylethylaldehyde is formed only in case of ethylbenzol. (*Ber. d. Chem. Ges.*, **22**, 1070.)

L. H. F.

#### Researches on Diazo Compounds. LUDWIG GATTERMANN.

Experiments which were performed with the intention of forming diphenyl from diazobenzol chloride by the action of metals, such as zinc dust, iron or copper powder, showed that copper at 0° C. reacts very strongly, but that no diphenyl but only chlorbenzol was formed. Following up this observation it may be stated, that in this manner also the amido group of aniline and of its homologues was replaced by bromine, cyanogen, the nitro and the sulphocyanogen groups. A fortunate accident finally showed that when diazobenzol sulphate was acted upon by powdered copper in the presence of alcohol, diphenyl was formed and *not* phenolether as anticipated. The cheaper zinc and iron *in the presence of alcohol*, react in the same manner to form diphenyl. (*Ber. d. Chem. Ges.*, **23**, 1218, 1890.)

L. H. F.

#### On Ethanedichinolyline. A. M. COMEY.

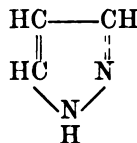
In order to give a wider application to Skraup's reaction, the author made paradiamidodibenzyl, nitrophenol, sulphuric acid

and glycerol react together. The base obtained crystallizes in colorless, hexagonal plates of melting point  $124^{\circ}$  C. The analysis led to the formula  $C_{20}H_{16}N_2$ . Since the two amido groups of diamidodibenzyl are in para position, the new base must be para-ethanedichinolyline, isomeric with Bulach's ethanedichinoline, melting at  $106.5^{\circ}$ . (*Ber. d. Chem. Ges.*, **23**, 1115, 1890.)

L. H. F.

#### Synthesis of Pyrazol. L. BALBIANO.

This body resulted from the reaction between hydrazinhydrate and epichlorhydrine. The analysis confirmed the formula  $C_3H_4N$ . Pyrazol crystallizes in hard, colorless needles. It dissolves in water to form a neutral solution. The odor is faintly suggestive of pyridine. Melting point:  $69.5-70^{\circ}$  C. Boiling point:  $186-188^{\circ}$  C., at 757.9 m. m. The properties of pyrazol correspond with those of a body prepared by Buchner from acetylenedicarbo-diazoacetic acid. This latter substance when heated to  $230-240^{\circ}$  C. decomposes into  $CO_2$  and  $C_3H_4N_2$ , the latter probably having the constitution :



(*Ber. d. Chem. Ges.*, **23**, 1103, 1890.)

L. H. F.

#### A New Lutidine. E. DÜRKOPF and H. GÖTTSCHE.

This base was obtained from dimethylpyridine carbo acid by splitting off  $CO_2$ . It is dried over KOH and boils then at  $169-170^{\circ}$  C. The analyses corresponded to a lutidine  $C_7H_8N$ . It is a clear, strongly refractive liquid of a mild, pleasant odor, characteristic of the  $\beta$ -compounds. It is more easily soluble in cold than in warm water. Spec. Grav. referred to water of  $+4^{\circ}$  C, is 0.9614, at  $0^{\circ}$  C. A two per cent. solution, oxidized in the cold furnished dinicotinic acid. This lutidine is therefore  $\beta\beta'$ -dimethylpyridine. (*Ber. d. Chem. Ges.*, **23**, 1113, 1890.)

L. H. F.



**On the Formation of the Quinolin Ring ; a Contribution to the Benzol Theory.** W. MARCKWALD.

v. Baeyer's researches (*Ann. Chem., Liebig*, **245**, 103 ; **251**, 257) show that the only three formulæ to be considered in regard to the constitution of benzol are, his own centric formula, Kekulé's and Dewar's.\* It was to be expected that the study of quinoline derivatives formed from aromatic diamines by one of the known synthetical methods, would lead to a decision in favor of one of these formulæ. All of the syntheses which the author has performed lead to phenanthrene ring formations, which speaks in favor of Kekulé's formula. (*Ber. d. Chem. Ges.*, **23**, 1015.)

L. H. F.

**On Indian Geranium Oil.** F. W. SEMMLER.

Fractional distillation at 17 m. m. pressure furnished 92 p. ct. of an oil boiling at 120.5 to 122.5 C. The analysis gave correct figures for a compound  $C_{10}H_{18}O$ , which proved to be geraniol. It does not congeal at  $-20^{\circ}C$ . The odor, which is still more agreeable in the refined than in crude oil, suggests the perfume of the pear or the rose. It is colorless and of Spec. Gr. 0.8900 at  $15^{\circ}C$ . The alcoholic nature of geraniol has been shown by Jacobsen. The optical methods, as well as the behavior toward iodine and bromine, indicate two ethylene linkings, and consequently this compound  $C_{10}H_{18}O$  cannot have a ring-formed constitution. It belongs to the fatty series,  $C_nH_{2n-2}O$ . Potassium permanganate oxidizes it to isovaleric acid. Under the influence of  $P_2O_5$ , terpenes and polyterpenes are formed. (*Ber. d. Chem. Ges.*, **23**, 1098, 1890.)

L. H. F.

**The Curves of Boiling Temperatures a Function of the Chemical Nature of Compounds.** M. WILDERMAN.

A simple rule for the determination of the boiling points of organic compounds at reduced pressure. Considering the great number of boiling point determinations at different pressures,

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\* In regard to this assertion see *Ber. d. Chem. Ges.*, **23**, 1276. It is expressly mentioned there, that Dewar's formula need *not* be considered.

L. H. F.

recorded by Regnault, Schumann, Anschütz and others, the author endeavored to find out whether the relation between pressure and boiling point of a substance has any connection with its chemical nature. About twenty homologous series were arranged and the following result was shown: Within tolerably wide limits of pressure, as between 1500 m. m. and 50 m. m., or, 760 m. m. and 12 m. m. the proportion of the absolute boiling point at  $M$  m. m. pressure to that of  $N$  m. m. is very nearly constant for all members of the homologous series. The tables given show that the *calculated* boiling points of a compound for an arbitrary pressure of  $N$  m. m. differ from the observed boiling point merely by a fraction of *one* degree. This is a difference which lies within the limits of error with which a boiling point can really be determined.

For members of the homologous series the following formula is an approximate expression:

$$\frac{T_a p}{T_a P} = \frac{T_b p}{T_b P} = \frac{T_c p}{T_c P} = D, (I)$$

in which  $a, b, c$  signify different members of the homologous series,  $p$  and  $P$  lower and higher pressures.

From this main formula five others of importance are derived. It follows from all of them, that the change of boiling point of a compound at a different pressure is really a function of its chemical nature. Bodies containing atoms of the same kind, and having the same constitution, which, consequently, are chemically equal, give the same numerical value. Different homologous series show considerable deviation. This is of great practical importance, particularly for compounds which decompose at ordinary pressure when the attempt to boil them is made. The formula given require merely the knowledge of *one* boiling point. (*Ber. d. Chem. Ges.*, 23, 1254, 1890.)

L. H. F.

## Abstracts of American Patents Relating to Chemistry.

(From the U. S. Patent Office Gazette.)

Issued May 27, 1890.

**428,587.**—Hydrocarbon burner. R. B. Avery and R. F. Smith.

**428,589.**—Diffusion apparatus. L. Boyer.

**428,610.**—Lubricant. S. Hopkins, Jr.

Consists of rod wax, lard and castor oil.

**428,614.**—Dyeing apparatus. C. L. Klauder.

**428,629.**—Substantive yellow dye. W. Pfltzinger.

Prepared by combining the diazo compounds of the thio derivatives of paratoluidine, metaxyldine, and pseudo cumidine or those of their sulpho-acids with the sulpho-acids of the thio derivatives of paratoluidine, metaxyldine and pseudo cumidine.

**428,638.**—Air pump. H. Schulze-Berge.

**428,654.**—Process of manufacturing thin sheets of nitrocellulose. E. N. Todd.

**428,659.**—Process of melting the ores of copper or other metals. C. Wessell.

The broken ore is mixed with potassium carbonate, sodium chloride, sodium nitrate and boric acid, and heated to the melting point.

**428,687.**—Composition for converting malleable cast iron into steel. W. J. Miles, Jr.

Consists of potassium ferrocyanide, potassium cyanide and potassium carbonate.

**428,747.**—Bottom for reducing furnaces. C. J. Eames.

Consists of dolomite, carbon, fluorspar, fire clay, fire sand and sufficient of a weak solution of sodium silicate to form a plastic mass.

**428,830.**—Apparatus for oxidizing or desulphurizing ores. E. M. Clark.

**428,834.**—Method of welding aluminium. M. Emme.

**428,955.**—Apparatus for the manufacture of gas. J. M. Rose.

**428,956.**—Apparatus for the manufacture of gas. J. M. Rose.

**429,054.**—Combined red pigment and paint base. J. P. Perkins.

Consists of an intimate mixture of ferric oxide and separated or precipitated silica.

**429,055.**—Process of treating slag for the production of red pigments. J. P. Perkins.

Silicious ferruginous slag is pulverized, treated with sulphuric acid and heated.

**429,056.**—Process of treating slag for the production of red pigments. J. P. Perkins.

Pulverized silicious ferruginous slag is heated with access of air, treated with sulphuric acid, and again heated.

**429,097.**—Process of manufacturing and bleaching pulp. C. Ramsey.

*Issued June 3d, 1890.*

**429,112.**—Filter. J. A. Bowden.

**429,117.**—Paving compound. D. C. Cregier.

Consists of coal tar, asphalt, metallic ore, sal-ammoniac, cement and lime.

**429,124.**—Apparatus for manufacturing malt. C. Fey.

**429,131.**—Process of printing calico. J. J. Hart.

The process consists, first in subjecting the fabric containing the lake or fixed color to a solution of developing reagent at a temperature below the point necessary to effect the chemical reaction between the lake or fixed color and the developing reagent, and then exposing the fabric containing the fixed color or lake and developing reagent to the action of heat to effect the chemical reaction.

**429,157.**—Antifriction alloy. S. Singley.

Consists of lead, antimony, tin, bismuth and silver.

**429,158.**—Antifriction alloy. S. Singley.

Consists of lead, antimony, tin, bismuth and aluminium.

**429,161.**—Washing compound. C. E. Starr.

Consists of oil of citronella, oleine laundry soap, alcohol, mineral oil, and water.

**429,225.**—Process of treating slag. St. G. T. C. Bryan.

**429,226.**—Method of treating slag. St. G. T. C. Bryan.

**429,248.**—Antifriction composition. S. Singley.

Consists of lead, antimony, tin, bismuth and graphite.

**429,249.**—Antifriction alloy. S. Singley.

Consists of lead, from 200–400 parts; antimony, 40–80 parts; tin, 15–30 parts, and bismuth,  $\frac{5}{8}$ – $1\frac{1}{4}$  parts.

**429,271.**—Apparatus for measuring and carbureting air or gas. F. H. Hambleton.

**429,309.**—Apparatus for the manufacture of gas. M. S. Greenough, E. C. Jones and W. R. Addicks.

**429,318.**—Gas meter. B. P. Moors.

**429,340.**—Oil filtering apparatus. J. Dooner.

**429,350.**—Red dye. G. Keorner.

The diazo dye stuff which results from the combination of two molecules of naphthionic acid with one molecule of the texrazo-derivative obtained by the action of nitrous acid on orthometatolidine, and which is

characterized by the following properties : it is a reddish brown powder easily soluble in hot water, slightly less soluble in cold, soluble in alcohol with a more yellowish color than in water, insoluble in benzine ; an aqueous solution (one one thousandth) upon treatment with an equal volume of acetic acid (thirty per cent.) yields a purple solution, and after standing a precipitate of the same color ; hydrochloric acid (twenty-five per cent.) gives at once a blue precipitate from the same solution, and the dye-stuff dyes cotton in the alkaline bath without a mordant a brilliant red color, with a slight yellow shade.

**429,886.**—Process of separating metallic impurities from graphite. M. W. Parrish.

**429,898.**—Regenerative gas burner. C. Westphal.

**429,414.**—Hydrocarbon burner. H. C. Brill.

**429,417.**—Apparatus for recovering soda. H. Burgess.

**429,428.**—Gas meter. J. W. Culmer.

**429,424.**—Gas meter. J. W. Culmer.

**429,426.**—Carbureting apparatus. W. Dawson.

**429,485.**—Detergent. J. J. Gilbert.

A compound for cleaning marble, etc., consisting of a mixture of muriatic acid, borax, soapstone, alum and sal-ammoniac.

**429,459.**—Apparatus for decolorizing, filtering, etc., liquids. B. Lavigne.

**429,482.**—Bottle stopper. W. L. Roorbach and G. W. Tucker.

**429,516.**—Manufacture of gunpowder. R. v. Freeden.

Gelatinized nitrocellulose, still containing the solvents, is stirred in water or steam, or both, until it is divided into grains. The grains are then removed and dried, and may be finished in the usual manner.

**429,522.**—Process of manufacturing sulphate of lead pigment. J. B. Hannay.

The process consists of the following successive operations : first, volatilizing suitable lead ore containing sulphur, and at the same time producing combustible gas mingled with the fumes of the mineral ; secondly, admitting air to a combustion chamber, so as to effect combustion of the gases, and thereby reheating and oxidizing the fumes ; thirdly, forcibly injecting the gaseous products and oxidized fumes through water or acidulated water in a condenser in which the sulphate of lead is deposited, and finally washing and drying the sulphate produced.

**429,523.**—Apparatus for the manufacture of sulphate of lead pigment. J. B. Hannay.

*Issued June 10th, 1890.*

**429,638.**—Process of manufacturing iron and steel. J. Reese.

The process consists in first decarburizing the metal while in a molten condition by subjecting it to the action of an oxidizing agent, and then

treating the decarburized metal with a calcareous agent and oxide of iron while maintained at a temperature above the fusion point of wrought iron.

**429,647.**—Process of disintegrating fibrous substances. G. M. Rose.

The crushed material is subjected to the action of a solution containing equal parts by weight of calcium oxychloride, potassium hydroxide, ammonium carbonate, and magnesium sulphate, at a temperature of 200° F.

**429,659.**—Enamel for coating bricks. J. Stiel.

Consists of a mixture of gravel, silicic acid, phosphorite, or analogous minerals, sodium carbonate, potash, cryolite, fluor spar, apatite, and metallic oxides for suitable coloring.

**429,675.**—Apparatus for generating oil gas. M. C. Burt.

**429,682.**—Apparatus for treating charcoal. R. V. F. de Guinon.

**429,692.**—Digestor. F. C. Lovejoy.

**429,744.**—Process of manufacturing iron or steel. A. J. Severance.

The process consists in adding to the metal while in a molten state a compound of borax, ammonium chloride, spathic iron and pumice, or their equivalents.

**429,777.**—Welding compound. A. J. Severance.

Consists of borax, pumice stone, salt, ammonium chloride, dolomite and spathic iron ore.

**429,791.**—Renovating fabrics. A. Mautner.

A cloth restoring composition for plush, velvet or other textile fabrics, composed of a solution of casein, ammonia, tartaric acid, alum, soap, gelatin, and an aniline or other dye.

**429,826.**—Apparatus for aging wines. L. Wagoner.

**429,892.**—Process of preventing the oxidation and deoxidation of copper when heated. G. W. Cummins.

The copper is heated in the presence of steam.

**430,055.**—Vulcanizing wood. W. C. Andrews.

Process consists in first placing the wood in a closed receptacle under high pressure of an aeriform fluid at ordinary temperature or without heat sufficient to boil the sap, and then, while retaining pressure, highly heating the contents.

*Issued June 17th, 1890.*

**430,120.**—Apparatus for filtering wine. H. B. Fischer and C. H. Fischer.

**430,127.**—Apparatus for carbonizing vegetable fibres. J. Illingworth.

**430,182.**—Method of preserving coffee, etc. P. Gassen.

The coffee, etc., is coated with shellac, wax or rosin, or mixtures of these.

**480,198.**—Apparatus for making chlorine. E. Solvay.

**480,199.**—Process of recarbonizing steel. A. Spannagel and F. Springorum.

A regulated stream of carbonaceous material is caused to mix with a stream of the molten metal from the ladle before its entrance into the ingot mold.

**480,212.**—Manufacture of explosives. H. S. Maxim.

The process consists in confining fibrous gun cotton in a receiver, exhausting the air from the same, then introducing vaporized acetone or its equivalent into the exhausted receiver and dissolving the gun cotton and then expelling the dissolved gun cotton by pressure from the receiver.

**480,213.**—Carburetor. H. Maxim.

**480,214.**—Recovering solvents from explosives. H. Maxim.

**480,250.**—Water color paint. G. S. Hodges and J. M. Tracy.

Consists of finely powdered water colors mixed with alcohol, Russian isinglass, gum arabic and glucose.

**480,379.**—Apparatus for the solution of gold, etc. S. H. Emmens.

**480,387.**—Apparatus for ozonizing air. J. C. Kennedy.

**480,393.**—Insecticide and method of making the same. J. M. A. Miller and P. McMaster.

The process of reducing sulphur to solution and of retaining it in solution, which consists in first adding to sulphur in a pulverized condition a solution of sodium chloride and potassium nitrate in water and thoroughly mixing the whole, then allowing the mass to stand until the sulphur is fairly or fully charged with the soda and potassa, then adding caustic soda to the mixture and agitating the mass, and subsequently allowing the whole to stand and cool.

**480,468.**—Regenerative gas lamp. F. W. Clark.

**480,508.**—Refractory compound for incandescent gas burners. J. E. Blomen.

Consists of an organic acid and magnesium salts, a mixture of magnesite and grape pomace or other suitable organic material, and magnesium oxide.

**480,516.**—Process of producing paper pulp from tobacco. H. Endemann.

The process consists in crushing the tobacco, steeping or boiling the crushed tobacco in water, treating the fibrous residue with a solution of aluminium sulphate under heat and pressure, then treating it with an alkaline substance.

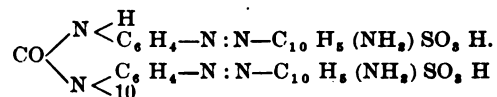
**480,533.**—Process of preparing diazo dyes. C. L. Müller.

The process consists in coupling together the molecules of certain amido-azo compounds by twos, by means of intermediaries, such as phosphene and thiophosgene or carbon bisulphide, in the presence of alkalies and alcohol, and the said amidoazo bodies are paramido-benzene-azo

bodies of the constitution represented by the formula  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 : \text{N} : \text{R}$ , in which the second element (the residue of which is denoted by R in the above formula) is a phenol, phenol-carboxylic acid or phenol-sulphonic acid, or an amido-sulphonic acid of the aromatic series, capable of combining with diazo compounds and forming azo bodies.

**480,584.**—Red to brown dye. C. L. Müller.

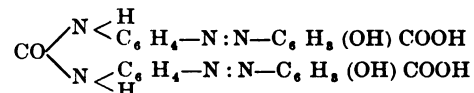
A pink to orange brown dye stuff, which is a sodium salt of an acid, which has the chemical constitution represented by the formula :



and which may be regarded as a disazo derivative of symmetrical diamido-diphenylurea, and is characterized by the following properties : It is a brownish red powder, soluble in water, alcohol and sulphuric acid, the aqueous and alcoholic solutions being of an orange red color ; from the former, hydrochloric acid throws down a dark bluish purple precipitate, whereas caustic soda produces no change ; the sulphuric acid solution is purple red in color, and water throws down from it a purple blue precipitate ; it dyes unmordanted cotton from the alkaline or soap both new shades, varying from flesh color to orange brown, according to the proportion of dye stuff used.

**480,585.**—Yellow dye. C. L. Müller.

It is chemically a sodium salt of an acid, the constitution of which is represented by the formula :



and which is to be regarded as a disazo derivative of symmetrical diamido-diphenylurea, and is characterized by the following properties : It is a dull yellow powder soluble in water, alcohol and sulphuric acid, the aqueous and alcoholic solutions being of a yellow color ; from the former hydrochloric acid throws down a dark red brown precipitate, while caustic soda solution turns it an orange yellow color ; the sulphuric acid solution is orange red in color, and water throws down from it a brown precipitate, and the dye stuff dyes unmordanted cotton in the boiling alkaline or soap bath a pure yellow color.

**480,586.**—Process of making butter. D. Gregory.

Consists in removing from yolk of egg the inclosing membrane and tread, agitating or heating the same with fresh milk, and incorporating the mixture with dairy butter until a homogeneous mass is obtained.

**480,595.**—Apparatus for making paper stock. J. D. Tompkins.



*Issued June 24th, 1890.*

**480,658.**—Process of producing plumbates of the alkaline earths. G. Kassner.

Consists in roasting in free air a mixture of lead oxide and the carbonate, hydroxide, or oxide of an alkaline earth. The lead oxide may be replaced by such salts of lead as are reduced to oxides by heat.

**480,728.**—Regenerative gas lamp. B. Zeitschel.

**480,725.**—Disinfectant. H. M. Baker.

A slowly dissolving double salt resulting from the combination of alkaline permanganates and silicates.

**480,784.**—Process of making alkaline carbonates and acetone.

The acetate of the alkaline earth is treated with the sulphate of an alkali, and the resulting alkaline acetate is subjected to distillation.

**480,807.**—Apparatus for the manufacture of gas. J. A. McCollum and B. F. Burt.

**480,812.**—Lubricant. J. J. Stock.

Consists of pulverized talc, beef tallow, paraffin oil, potash lye, vermilion red, and oil of myrbane.

**480,850.**—Cleansing compound. S. V. Harbaugh.

A combination of coal ashes which have been sifted and desiccated with a due proportion of water, salts of tartar, chloride of lime, and carbonate of ammonia.

**480,923.**—Apparatus for dyeing. C. Corron.

**480,958.**—Vulcanized plastic compound. W. Kiel.

Consists of crude rubber, sulphur, and mineral oil.

**480,959.**—Process of manufacturing vulcanized plastic compounds. W. Kiel.

Consists in mixing together sulphur, rubber, and oil, the sulphur being in the proportion of not less than about 80 per cent. of the rubber, by weight, and vulcanizing the compound with an initial temperature of not less than 300° F.

**480,975.**—Red dye. C. Schraube.

The disulpho acid of the red basic naphthalene coloring matter, called "rosinduline," which has the chemical composition represented by the formula,  $C_{10}H_7N_2(SO_3H)_2$ , and which is characterized by the following properties : It is a red crystalline powder soluble in concentrated sulphuric acid, giving a bright green solution ; it is slightly soluble in cold water, more readily soluble in boiling water ; its alkaline salts are crystalline, and soluble in hot, slightly soluble in cold water ; the sodium and potassium salts crystallize from hot solutions on cooling after the addition of common salt ; the free acid dyes animal fibre a bright red color in the acid bath.

*Issued July 1st, 1890.*

**481,026.**—Process of manufacturing red lead. M. Alsberg.

The process consists in incorporating lead nitrate into the material (oxide or carbonate of lead), and exposing the resulting mixture to heat sufficiently high to first drive off any water that may be contained in it, and then to decompose the lead nitrate, thereby furnishing oxygen for the formation of minium.

**481,044.**—Process of making antimony fluorides. O. O. B. Froelich.

Antimony fluoride and its soluble compounds are prepared by treating a mixture of antimony ore, alkaline nitrates and fluor spar with oil of vitriol, extracting the soluble matter with water, neutralizing the solution with alkalis, and evaporating to crystallization.

**481,059.**—Carburetor. P. Keller.

**481,104.**—Protective covering for electric cables. J. H. Cheever.

Consists of rubber, plumbago, asbestos and sulphur.

**481,182.**—Test tube. J. C. Wharton.

A test tube having a ground or roughened external surface.

**481,229.**—Filtering apparatus. O. H. Jewell and W. M. Jewell.

**481,248.**—Obtaining acetic acid and methyl alcohol. F. C. Alkier.

The process of recovering the methyl alcohol and acetic acid from the waste wash water or lye in the manufacture of paper from wood pulp, which consists in concentrating the lye by repeated use, neutralizing by means of an alkali as concentration proceeds, recovering the methyl alcohol from the concentrated solution by distillation, evaporating the residuary liquid to dryness, and obtaining the acetic acid from the acetate by distillation with an acid.

**481,268.**—Paint. H. Le Bates and E. P. Lawrence.

Consists of a color, and a base composed of a soluble chloride and nitrate, alcohol, molasses and water.

**481,297.**—Azo color. J. Walter.

Aniline is dissolved in hydrochloric acid and water. When heated to a proper degree sodium nitrite is added. This solution is poured, while stirring, into an alkaline solution of solicylic acid. The whole is then precipitated with an acid and filtered. The dry product of the combination is dissolved in sulphuric acid. Then a mixture of nitric acid and sulphuric acid is added. The liquid thus obtained is poured in water and filtered.

**481,386.**—Apparatus for distilling oil. T. McGowan.

**481,404.**—Rosinduline sulpho acid. C. Schraube.

Is a red amorphous powder soluble in concentrated sulphuric acid, giving a bright green solution; it is readily soluble in cold water and soluble in alcohol and yields amorphous alkaline salts, which are also readily soluble in cold water and cannot be precipitated by common salt. It dyes animal fibre in the acid bath a bright red color.

**481,407.**—Process of preserving meat, etc. W. Smith.

Meat, etc., is sealed in vessels in sterilized air.

**481,426.**—Method of making fabrics. J. I. Wood.

The process consists in first, soaking a fibrous material in a bath of rosin soap; second, drying the material; third, subjecting the material while yet damp to a bath of zinc chloride; fourth, passing it over hot rollers; fifth, washing it; sixth, drying it; seventh, coating it with oil; and lastly, passing it between calenders.

**481,429.**—Manufacture of plates and slabs for building purposes. A. van Berkel.

Consists of burned magnesium carbonate or magnesite, raw paper stuff, peat, sand or other finely divided material, and a solution of fluoric silicate containing vegetable flour.

**481,448.**—Filter, T. S. E. Dixon.

**481,472.**—Process of making thiooxydiphenylamine. M. Lange.

A salt of metaoxydiphenylamine is heated with water, sulphur and an alkali or alkaline carbonate, or with a sulphide or polysulphide of alkali. It is a light yellow powder, easily soluble in alkalies, soluble in alcohol and acetic acid, and also, though more difficultly, soluble in alkaline carbonates; insoluble in water and benzene. The solutions are of a yellow color. When heated the substance becomes brown and melts at about 155° C.

**481,505.**—Making white lead. P. Bronner.

The process consists in converting normal lead sulphate into a basic salt, such as  $2 \text{Pb SO}_4$ ,  $\text{Pb (HO)}_2$ , or  $3 \text{Pb SO}_4$ ,  $\text{Pb (HO)}_2$ —by heating it with caustic alkaline lyes, and then heating the basic salt, with a solution of an excess of sodium carbonate.

**481,535.**—Apparatus for the manufacture of gas. W. J. Taylor.

**481,541.**—Blue dye. T. Reissig.

Is produced by the condensation of alphanaphthylamine, with the mononitroso compound of diethylmetaamidophenol, and has the following properties: It appears in the form of a dark, crystalline, bronze-like powder, soluble in both alcohol and water with a blue color, the alcohol solution turning red upon the addition of caustic alkali, and becoming decolorized by subsequent heating with zinc dust, but quickly resuming its red color upon the access of air, while the aqueous solution of the coloring matter is precipitated by caustic alkalies, the precipitate consisting of the free coloring base, being soluble in sulphuric ether, with a yellow color and a yellow fluorescence, and it produces upon animal fibres without the aid of a mordant in a neutral or slightly acid bath, and upon vegetable fibres, with the aid of a tannin mordant, bright blue shades, similar to those of methylene blue.

*(Issued July 8th, 1890.)*

**481,646.**—Composition for the soles of boots or shoes. W. A. Burrows.

Consists of leather flock, water, gelatine and chrome alum.

**481,780.**—Process of obtaining meat extract. J. Van Ruymbeke.

**481,795.**—Apparatus for testing the burning qualities of oil. F. W. Arvine.

**481,912.**—Process of making aluminium. C. Netto.

Cryolite is melted with a flux, and an alkaline metal suddenly introduced.

**481,982.**—Apparatus for the manufacture of gas. W. T. Bate.

**481,987.**—Apparatus for extracting oil. H. A. A. Dombrain.

**481,985.**—Fire extinguishing compound. C. M. Martin.

Consists of sodium chloride, sodium thiosulphate, ammonium chloride, magnesium sulphate, magnesium chloride, calcium oxide and ferrous oxide, mixed and dissolved in water.

**481,986.**—Purifying salt. E. K. Mitting.

The salt recovered from spent soap lye is washed with a saturated solution of salt, to which a small proportion of alkali has been added, and a similar saturated solution containing acid.

W. R.



## THE NEWPORT MEETING.

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In accordance with the provisions of the revised constitution of the American Chemical Society (Art. VII, Section 2), and in pursuance of a resolution of the Society passed at the regular meeting, June 6, 1890, the Board of Directors, on July 22, called a general meeting of the Society at Newport, R. I., Aug. 6 and 7, 1890. Owing to the unavoidable shortness of the notice given, it was feared that no adequate attendance of chemists could be secured, and the meeting was regarded more as an introduction to a series of general meetings to be held hereafter than as a test of the favor which might be expected for the new plan from the chemists of the country.

The meeting has been a great success, however, and it was regarded by those present as fully equal, both in general interest and in scientific gain, to any gathering of chemists ever held in America.

Over forty chemists attended the meeting, and, together with friends who accompanied them and citizens of Newport who took part in the entertainment of the visitors, made the occasion an attractive one in its social as well as in its professional aspect.

Seventeen papers were read and these, with the discussions upon them and the general business of the meeting, fully occupied the morning sessions. A list of these papers is given in the programme, page 252. The time of the meeting was so divided as to allow the hours from 10 A. M. to 1 P. M. to be given to the reading of papers, business, etc. At 1 P. M. a luncheon, provided each day through the kindness of the local committee, was served in a room adjoining the hall.

At 2 P. M. the visitors were taken upon steam launches, provided by the local committee to points of interests about Newport harbor and the afternoon spent in sailing each day was a pleasant relaxation after the work of the morning. Wednesday evening was

given up to social intercourse amongst the visitors, and on Thursday evening the reception given by Prof. J. P. Cooke was a fitting conclusion to the long series of courtesies offered by the local committee.

During the meeting a collection of chemical apparatus was exhibited in a room adjoining the hall. It is hoped that at general meetings in future this feature will be much more fully developed. Invitations were sent to many dealers in chemical apparatus, but the notice of the meeting was too short for proper efforts in this direction.

The meeting was opened Wednesday, August 6th, at 10 A. M. (See minutes of meeting.)

#### WEDNESDAY AFTERNOON.

Members and invited guests met at the Ferry at 2:30, and were taken on a government launch to the United States Naval Torpedo Station, situated on an island in the harbor opposite Newport, where they were met by Commander T. F. Jewell, U. S. N., in charge of the Torpedo Station, through whose courtesy the museum, laboratory and shops of the station were opened to the party. The historical collection of torpedoes and models was shown, including torpedoes of modern construction, ready for use. At the laboratory Prof. C. E. Munroe explained the action of a number of high explosives and showed the results of experiments in crushing and rupturing of metallic plates. Afterwards several submarine torpedoes were exploded in the harbor, and a series of tests with high explosives was made. Discs of compressed gun cotton, dynamite, etc., were detonated upon plates of wrought iron; compressed gun cotton was partly burned in an open fire and then exploded by detonation. A naked disc of gun cotton bearing the impressed letters A. C. S. was detonated upon an iron plate, and the letters were shown to be clearly impressed upon the metal afterwards. A "necklace" of discs of gun cotton was hung about the top of a wooden post twelve inches in cross section and the timber was cut off squarely by detonation of the cotton.

At 4 o'clock the party were taken to the United States Naval Training Station, also located on an island in the harbor, where,

through the courtesy of Capt. Stanton, U. S. N., commanding, they witnessed a parade of the battalion of boys belonging to the station. Afterward they were entertained at the officers' quarters, and, before leaving, were shown the barracks and drill room under the guidance of Surgeon C. A. Siegfried, U. S. N. The return to Newport was made at 6 P. M.

## THURSDAY, AUG. 7.

## MORNING.

The meeting was called to order at 10 o'clock. (See minutes of meeting.)

## AFTERNOON.

2 o'Clock.—Through the courtesy of the local committee an excursion in Newport harbor was provided. The larger portion of the visitors were taken on a government launch under the guidance of Major Livermore, and after sailing about the harbor, were landed at Fort Adams at 4 P. M. A smaller party took passage on the Herreshoff torpedo boat Stiletto, which was kindly placed at their service by Commander Jewell, and made a tour of about thirty miles around the island of Conanicut. The great speed of the little boat and the perfection of her machinery called forth much enthusiastic comment. The Stiletto reached Fort Adams before four o'clock and the united party of visitors were taken to the artillery parade ground, where, through the courtesy of Col. John Mendenhall, commanding, they spent an hour in watching the evolutions of a battery of artillery, consisting of four field pieces, with its full complement of men and horses. After a number of rounds had been fired by the battery the guests were permitted to inspect the mechanism of the breech loading guns. Returning to the boats, a stop was made to examine the large guns of the Fort.

The party returned to Newport at 6 o'clock.

The reception given to the chemists attending the meeting by Prof. J. P. Cooke, at his home, cor. Gibbs avenue and Beach street, Newport, was very fully attended. Many specimens of meteorites from the collection of Prof. Cooke were shown during the evening.



The following is a list of chemists who attended the meeting, as taken from the register kept at the office of Mr. A. O. D. Taylor, of the local committee :

- Prof. John H. Appleton, Brown University, Providence, R. I.
- Elias H. Bartley, M. D., Brooklyn, N. Y.
- Marcus Benjamin, Ph. D., New York.
- William B. Bentley.
- Prof. A. A. Breneman, New York.
- Edwin C. Calder, Providence, R. I.
- Prof. C. F. Chandler, Columbia College, New York.
- Prof. F. W. Clarke, chief chemist, U. S. Geological Survey, Washington, D. C.
- Prof. Josiah P. Cooke, Harvard University, Cambridge, Mass.
- William D. Crumbie, U. S. Laboratory, New York.
- Prof. A. E. Dolbear, Tuft's College, Medford, Mass.
- Prof. C. A. Doremus, City College, New York.
- Dr. L. H. Friedburg, City College, New York.
- Dr. Wolcott Gibbs, Harvard University, Cambridge, Mass.
- Martin L. Griffin, Holyoke, Mass.
- Prof. Albert C. Hale, Brooklyn, N. Y.
- Dr. A. P. Hallock, New York.
- Dr. Walter H. Kent, Board of Health, Brooklyn, N. Y.
- Major W. R. Livermore, U. S. A., Newport, R. I.
- Dr. Morris Loeb, Clark University, Worcester, Mass.
- Prof. W. M. McMurtrie, New York.
- Prof. E. W. Morley, Western Reserve University, Cleveland, Ohio.
- Prof. Charles E. Munroe, U. S. Naval Torpedo Station, Newport, R. I.
- E. B. Newbury, Cornell University, Ithaca, New York.
- Lyman C. Newell, Pawtucket, R. I.
- C. F. Parker, U. S. A., Newport, R. I.
- G. W. Patterson, U. S. Torpedo Station, Newport, R. I.
- Charles M. Perry, Providence, R. I.
- Dr. C. A. Pitkin, Thayer Academy, South Braintree, Mass.
- Lucius Pitkin, Ph. B., New York.
- William R. Potter, Providence, R. I.
- Frederic Read, New York.

William Rupp, New York.  
Prof. A. H. Sabine, Long Island City, New York.  
Edward Sherer, U. S. Laboratory, New York.  
C. A. Siegfried, Surgeon U. S. N., Newport, R. I.  
Herbert E. Smith, New Haven, Conn.  
Frank E. Thompson, Head Master Rogers High School, Newport, R. I.  
J. H. Wainwright, Ph. B., U. S. Laboratory, New York.  
Lieut. Willoughby Walke, 2d U. S. Artillery, Fort Monroe, Va.  
Prof. Elwyn Waller, Columbia College, New York.  
Arthur W. Wellington, Newport, R. I.  
Dr. H. J. Wheeler, Experiment Station, Kingston, R. I.

## LOCAL COMMITTEE.

Prof. Charles E. Munroe, *Chairman*.  
Dr. J. P. Cooke.  
Dr. Wolcott Gibbs.  
Major T. K. Gibbs.  
Commander T. F. Jewell, U. S. N.  
Major W. R. Livermore, Eng. Corps, U. S. A.  
Dr. C. A. Siegfried, Surgeon, U. S. N.  
Dr. T. A. Kenefick.  
A. O'D. Taylor, Esq., Secretary Newport Natural History Society.  
C. A. Pitkin, Ph. D.  
F. E. Thompson, Head Master Rogers High School.  
Lt. C. DeW. Wilcox, 2d Art., U. S. A.  
F. Bradley, D. M. D.  
G. W. Patterson, Esq.

## COMMITTEE OF ARRANGEMENTS.

Prof. A. A. Breneman, *Chairman*.  
Prof. C. F. Chandler.  
William Rupp.  
C. F. McKenna.  
J. F. Geisler.

*Issued June 24th, 1890.*

**480,658.**—Process of producing plumbates of the alkaline earths. G. Kassner.

Consists in roasting in free air a mixture of lead oxide and the carbonate, hydroxide, or oxide of an alkaline earth. The lead oxide may be replaced by such salts of lead as are reduced to oxides by heat.

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A slowly dissolving double salt resulting from the combination of alkaline permanganates and silicates.

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The acetate of the alkaline earth is treated with the sulphate of an alkali, and the resulting alkaline acetate is subjected to distillation.

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Consists of pulverized talc, beef tallow, paraffin oil, potash lye, vermilion red, and oil of myrbane.

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A combination of coal ashes which have been sifted and desiccated with a due proportion of water, salts of tartar, chloride of lime, and carbonate of ammonia.

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**480,958.**—Vulcanized plastic compound. W. Kiel.

Consists of crude rubber, sulphur, and mineral oil.

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Consists in mixing together sulphur, rubber, and oil, the sulphur being in the proportion of not less than about 80 per cent. of the rubber, by weight, and vulcanizing the compound with an initial temperature of not less than 300°F.

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*Issued July 1st, 1890.*

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The process consists in incorporating lead nitrate into the material (oxide or carbonate of lead), and exposing the resulting mixture to heat sufficiently high to first drive off any water that may be contained in it, and then to decompose the lead nitrate, thereby furnishing oxygen for the formation of minium.

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Antimony fluoride and its soluble compounds are prepared by treating a mixture of antimony ore, alkaline nitrates and fluor spar with oil of vitriol, extracting the soluble matter with water, neutralizing the solution with alkalies, and evaporating to crystallization.

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Consists of rubber, plumbago, asbestos and sulphur.

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A test tube having a ground or roughened external surface.

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The process of recovering the methyl alcohol and acetic acid from the waste wash water or lye in the manufacture of paper from wood pulp, which consists in concentrating the lye by repeated use, neutralizing by means of an alkali as concentration proceeds, recovering the methyl alcohol from the concentrated solution by distillation, evaporating the residuary liquid to dryness, and obtaining the acetic acid from the acetate by distillation with an acid.

**481,268.**—Paint. H. Le Bates and E. P. Lawrence.

Consists of a color, and a base composed of a soluble chloride and nitrate, alcohol, molasses and water.

**481,297.**—Azo color. J. Walter.

Aniline is dissolved in hydrochloric acid and water. When heated to a proper degree sodium nitrite is added. This solution is poured, while stirring, into an alkaline solution of salicylic acid. The whole is then precipitated with an acid and filtered. The dry product of the combination is dissolved in sulphuric acid. Then a mixture of nitric acid and sulphuric acid is added. The liquid thus obtained is poured in water and filtered.

**481,386.**—Apparatus for distilling oil. T. McGowan.

**481,404.**—Rosinduline sulpho acid. C. Schraube.

Is a red amorphous powder soluble in concentrated sulphuric acid, giving a bright green solution; it is readily soluble in cold water and soluble in alcohol and yields amorphous alkaline salts, which are also readily soluble in cold water and cannot be precipitated by common salt. It dyes animal fibre in the acid bath a bright red color.

**481,407.**—Process of preserving meat, etc. W. Smith.

Meat, etc., is sealed in vessels in sterilized air.

**481,426.**—Method of making fabrics. J. I. Wood.

The process consists in first, soaking a fibrous material in a bath of rosin soap; second, drying the material; third, subjecting the material while yet damp to a bath of zinc chloride; fourth, passing it over hot rollers; fifth, washing it; sixth, drying it; seventh, coating it with oil; and lastly, passing it between calenders.

**481,429.**—Manufacture of plates and slabs for building purposes. A. van Berkel.

Consists of burned magnesium carbonate or magnesite, raw paper stuff, peat, sand or other finely divided material, and a solution of fluoric silicate containing vegetable flour.

**481,448.**—Filter, T. S. E. Dixon.

**481,472.**—Process of making thiooxydiphenylamine. M. Lange.

A salt of metaoxydiphenylamine is heated with water, sulphur and an alkali or alkaline carbonate, or with a sulphide or polysulphide of alkali. It is a light yellow powder, easily soluble in alkalies, soluble in alcohol and acetic acid, and also, though more difficultly, soluble in alkaline carbonates; insoluble in water and benzene. The solutions are of a yellow color. When heated the substance becomes brown and melts at about 155° C.

**481,505.**—Making white lead. P. Bronner.

The process consists in converting normal lead sulphate into a basic salt, such as  $2\text{Pb SO}_4$ ,  $\text{Pb (HO)}_2$ , or  $3\text{Pb SO}_4$ ,  $\text{Pb (HO)}_2$ —by heating it with caustic alkaline lyes, and then heating the basic salt, with a solution of an excess of sodium carbonate.

**481,585.**—Apparatus for the manufacture of gas. W. J. Taylor.

**481,541.**—Blue dye. T. Reissig.

Is produced by the condensation of alphanaphthylamine, with the mononitroso compound of diethylmetaamidophenol, and has the following properties: It appears in the form of a dark, crystalline, bronze-like powder, soluble in both alcohol and water with a blue color, the alcohol solution turning red upon the addition of caustic alkali, and becoming decolorized by subsequent heating with zinc dust, but quickly resuming its red color upon the access of air, while the aqueous solution of the coloring matter is precipitated by caustic alkalies, the precipitate consisting of the free coloring base, being soluble in sulphuric ether, with a yellow color and a yellow fluorescence, and it produces upon animal fibres without the aid of a mordant in a neutral or slightly acid bath, and upon vegetable fibres, with the aid of a tannin mordant, bright blue shades, similar to those of methylene blue.

*(Issued July 8th, 1890.)*

**481,646.**—Composition for the soles of boots or shoes. W. A. Burrows.

Consists of leather flock, water, gelatine and chrome alum.

**481,780.**—Process of obtaining meat extract. J. Van Ruymbeke.

**481,795.**—Apparatus for testing the burning qualities of oil. F. W. Arvine.

**481,912.**—Process of making aluminium. C. Netto.

Cryolite is melted with a flux, and an alkaline metal suddenly introduced.

**481,982.**—Apparatus for the manufacture of gas. W. T. Bate.

**481,987.**—Apparatus for extracting oil. H. A. A. Dombrain.

**481,985.**—Fire extinguishing compound. C. M. Martin.

Consists of sodium chloride, sodium thiosulphate, ammonium chloride, magnesium sulphate, magnesium chloride, calcium oxide and ferric oxide, mixed and dissolved in water.

**481,986.**—Purifying salt. E. K. Mitting.

The salt recovered from spent soap lye is washed with a saturated solution of salt, to which a small proportion of alkali has been added, and a similar saturated solution containing acid.

W. R.



## THE NEWPORT MEETING.

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In accordance with the provisions of the revised constitution of the American Chemical Society (Art. VII, Section 2), and in pursuance of a resolution of the Society passed at the regular meeting, June 6, 1890, the Board of Directors, on July 22, called a general meeting of the Society at Newport, R. I., Aug. 6 and 7, 1890. Owing to the unavoidable shortness of the notice given, it was feared that no adequate attendance of chemists could be secured, and the meeting was regarded more as an introduction to a series of general meetings to be held hereafter than as a test of the favor which might be expected for the new plan from the chemists of the country.

The meeting has been a great success, however, and it was regarded by those present as fully equal, both in general interest and in scientific gain, to any gathering of chemists ever held in America.

Over forty chemists attended the meeting, and, together with friends who accompanied them and citizens of Newport who took part in the entertainment of the visitors, made the occasion an attractive one in its social as well as in its professional aspect.

Seventeen papers were read and these, with the discussions upon them and the general business of the meeting, fully occupied the morning sessions. A list of these papers is given in the programme, page 252. The time of the meeting was so divided as to allow the hours from 10 A. M. to 1 P. M. to be given to the reading of papers, business, etc. At 1 P. M. a luncheon, provided each day through the kindness of the local committee, was served in a room adjoining the hall.

At 2 P. M. the visitors were taken upon steam launches, provided by the local committee to points of interests about Newport harbor and the afternoon spent in sailing each day was a pleasant relaxation after the work of the morning. Wednesday evening was



given up to social intercourse amongst the visitors, and on Thursday evening the reception given by Prof. J. P. Cooke was a fitting conclusion to the long series of courtesies offered by the local committee.

During the meeting a collection of chemical apparatus was exhibited in a room adjoining the hall. It is hoped that at general meetings in future this feature will be much more fully developed. Invitations were sent to many dealers in chemical apparatus, but the notice of the meeting was too short for proper efforts in this direction.

The meeting was opened Wednesday, August 6th, at 10 A. M. (See minutes of meeting.)

#### WEDNESDAY AFTERNOON.

\* Members and invited guests met at the Ferry at 2:30, and were taken on a government launch to the United States Naval Torpedo Station, situated on an island in the harbor opposite Newport, where they were met by Commander T. F. Jewell, U. S. N., in charge of the Torpedo Station, through whose courtesy the museum, laboratory and shops of the station were opened to the party. The historical collection of torpedoes and models was shown, including torpedoes of modern construction, ready for use. At the laboratory Prof. C. E. Munroe explained the action of a number of high explosives and showed the results of experiments in crushing and rupturing of metallic plates. Afterwards several submarine torpedoes were exploded in the harbor, and a series of tests with high explosives was made. Discs of compressed gun cotton, dynamite, etc., were detonated upon plates of wrought iron; compressed gun cotton was partly burned in an open fire and then exploded by detonation. A naked disc of gun cotton bearing the impressed letters A. C. S. was detonated upon an iron plate, and the letters were shown to be clearly impressed upon the metal afterwards. A "necklace" of discs of gun cotton was hung about the top of a wooden post twelve inches in cross section and the timber was cut off squarely by detonation of the cotton.

At 4 o'clock the party were taken to the United States Naval Training Station, also located on an island in the harbor, where,

through the courtesy of Capt. Stanton, U. S. N., commanding, they witnessed a parade of the battalion of boys belonging to the station. Afterward they were entertained at the officers' quarters, and, before leaving, were shown the barracks and drill room under the guidance of Surgeon C. A. Siegfried, U. S. N. The return to Newport was made at 6 P. M.

## THURSDAY, AUG. 7.

## MORNING.

The meeting was called to order at 10 o'clock. (See minutes of meeting.)

## AFTERNOON.

2 o'clock.—Through the courtesy of the local committee an excursion in Newport harbor was provided. The larger portion of the visitors were taken on a government launch under the guidance of Major Livermore, and after sailing about the harbor, were landed at Fort Adams at 4 P. M. A smaller party took passage on the Herreshoff torpedo boat Stiletto, which was kindly placed at their service by Commander Jewell, and made a tour of about thirty miles around the island of Conanicut. The great speed of the little boat and the perfection of her machinery called forth much enthusiastic comment. The Stiletto reached Fort Adams before four o'clock and the united party of visitors were taken to the artillery parade ground, where, through the courtesy of Col. John Mendenhall, commanding, they spent an hour in watching the evolutions of a battery of artillery, consisting of four field pieces, with its full complement of men and horses. After a number of rounds had been fired by the battery the guests were permitted to inspect the mechanism of the breech loading guns. Returning to the boats, a stop was made to examine the large guns of the Fort.

The party returned to Newport at 6 o'clock.

The reception given to the chemists attending the meeting by Prof. J. P. Cooke, at his home, cor. Gibbs avenue and Beach street, Newport, was very fully attended. Many specimens of meteorites from the collection of Prof. Cooke were shown during the evening.

The following is a list of chemists who attended the meeting, as taken from the register kept at the office of Mr. A. O. D. Taylor, of the local committee :

- Prof. John H. Appleton, Brown University, Providence, R. I.
- Elias H. Bartley, M. D., Brooklyn, N. Y.
- Marcus Benjamin, Ph. D., New York.
- William B. Bentley.
- Prof. A. A. Breneman, New York.
- Edwin C. Calder, Providence, R. I.
- Prof. C. F. Chandler, Columbia College, New York.
- Prof. F. W. Clarke, chief chemist, U. S. Geological Survey, Washington, D. C.
- Prof. Josiah P. Cooke, Harvard University, Cambridge, Mass.
- William D. Crumbie, U. S. Laboratory, New York.
- Prof. A. E. Dolbear, Tuft's College, Medford, Mass.
- Prof. C. A. Doremus, City College, New York.
- Dr. L. H. Friedburg, City College, New York.
- Dr. Wolcott Gibbs, Harvard University, Cambridge, Mass.
- Martin L. Griffin, Holyoke, Mass.
- Prof. Albert C. Hale, Brooklyn, N. Y.
- Dr. A. P. Hallock, New York.
- Dr. Walter H. Kent, Board of Health, Brooklyn, N. Y.
- Major W. R. Livermore, U. S. A., Newport, R. I.
- Dr. Morris Loeb, Clark University, Worcester, Mass.
- Prof. W. M. McMurtrie, New York.
- Prof. E. W. Morley, Western Reserve University, Cleveland, Ohio.
- Prof. Charles E. Munroe, U. S. Naval Torpedo Station, Newport, R. I.
- E. B. Newbury, Cornell University, Ithaca, New York.
- Lyman C. Newell, Pawtucket, R. I.
- C. F. Parker, U. S. A., Newport, R. I.
- G. W. Patterson, U. S. Torpedo Station, Newport, R. I.
- Charles M. Perry, Providence, R. I.
- Dr. C. A. Pitkin, Thayer Academy, South Braintree, Mass.
- Lucius Pitkin, Ph. B., New York.
- William R. Potter, Providence, R. I.
- Frederic Read, New York.

William Rupp, New York.  
Prof. A. H. Sabine, Long Island City, New York.  
Edward Sherer, U. S. Laboratory, New York.  
C. A. Siegfried, Surgeon U. S. N., Newport, R. I.  
Herbert E. Smith, New Haven, Conn.  
Frank E. Thompson, Head Master Rogers High School, Newport, R. I.  
J. H. Wainwright, Ph. B., U. S. Laboratory, New York.  
Lieut. Willoughby Walke, 2d U. S. Artillery, Fort Monroe, Va.  
Prof. Elwyn Waller, Columbia College, New York.  
Arthur W. Wellington, Newport, R. I.  
Dr. H. J. Wheeler, Experiment Station, Kingston, R. I.

## LOCAL COMMITTEE.

Prof. Charles E. Munroe, *Chairman*.  
Dr. J. P. Cooke.  
Dr. Wolcott Gibbs.  
Major T. K. Gibbs.  
Commander T. F. Jewell, U. S. N.  
Major W. R. Livermore, Eng. Corps, U. S. A.  
Dr. C. A. Siegfried, Surgeon, U. S. N.  
Dr. T. A. Kenefick.  
A. O'D. Taylor, Esq., Secretary Newport Natural History Society.  
C. A. Pitkin, Ph. D.  
F. E. Thompson, Head Master Rogers High School.  
Lt. C. DeW. Wilcox, 2d Art., U. S. A.  
F. Bradley, D. M. D.  
G. W. Patterson, Esq.

## COMMITTEE OF ARRANGEMENTS.

Prof. A. A. Breneman, *Chairman*.  
Prof. C. F. Chandler.  
William Rupp.  
C. F. McKenna.  
J. F. Geisler.

MINUTES OF THE FIRST GENERAL MEETING OF THE  
AMERICAN CHEMICAL SOCIETY, HELD AT  
MASONIC HALL, NEWPORT, R. I.,  
AUGUST 6 AND 7, 1890.

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FIRST DAY—AUGUST 6.

The meeting was called to order at 10.15 A.M. by Prof. Charles F. Chandler, chairman. Prof. Albert C. Hale was appointed secretary.

An address of welcome in behalf of the citizens of Newport was then presented by Col. John Hare Powel, Ex-Mayor of Newport, and a descendant of Dr. Robert Hare of Philadelphia.

In the response by the Chairman, Prof. Chandler, a brief resumé of the organization and history of the Society was given, and special reference was made to the recent revision of the Constitution, under which this first general meeting was called.

Letters of regret were then read from the following members, who were unable to attend the meeting, viz.:

President, H. B. Nason, Troy, N. Y.; Dr. F. A. Genth, Philadelphia; Dr. T. Sterry Hunt, New York; Prof. Henry Morton, Hoboken.

The reading of papers being in order, the following papers were presented:

“Determination of the Strength of various High Explosives.”—Willoughby Walke.

“The Volumetric Composition of Water.”—E. W. Morley.

“On Carbon as an Impurity Affecting the Determination of the Atomic Weight of Hydrogen.”—E. W. Morley.

“A New Form of Air Thermometer for Technical Uses.”—A. H. Sabine.

“A New Apparatus and an Improved Method for the Estimation of Urea.”—E. H. Bartley.

“On Resins.”—L. H. Friedburg.

The meeting was adjourned at 12.50.

## SECOND DAY—AUGUST 7.

The meeting was called to order by the Chairman, Prof. C. F. Chandler at 10.15 A.M.

An announcement was made by Prof. C. E. Munroe regarding the afternoon excursion on the U. S. Torpedo boat "Stiletto."

An invitation was given the members and guests of the Society, by Prof. Josiah P. Cooke, to attend an informal reception at his home, Gibbs ave. and Beach street, Thursday evening between 7 and 9 o'clock.

On motion of Prof. A. A. Breneman, Chairman of the Committee of Arrangements, the following votes of thanks were extended :

- I.—To the Members of the Local Committee.
- II.—To Col. John Mendenhall, U. S. A., commanding Fort Adams,  
Capt. Oscar F. Stanton, U. S. N., commanding U. S.  
Naval Training Station,  
Com. T. F. Jewell, U. S. N., commanding Torpedo Station,  
Major W. R. Livermore, Eng. Corps, U. S. A.
- III.—To the Newport Natural History Society for the offer of its  
rooms for the meeting.
- IV.—To the Citizens of Newport for their kindness and courtesy.

The Chairman then announced an informal discussion regarding the more general organization of chemists in America. On motion of Dr. Waller, it was voted that all chemists present be invited to present their views freely, and have all privileges of discussion and voting upon the subject.

After some introductory remarks by Prof. Chandler, Prof. Clarke opened the discussion by presenting a brief history of the new movement for a proposed "Continental" Society. He was followed by Dr. Wolcott Gibbs, Dr. J. P. Cooke, Maj. Livermore, Dr. C. A. Doremus, Dr. Morris Loeb, Prof. A. H. Sabine, Prof. A. A. Breneman, Prof. Albert C. Hale, Dr. Waller, and others. Dr. Waller moved that the Chair appoint three members of the American Chemical Society to represent that society at a conference of representatives of various societies and chemists in this country, the time and place of said conference to be left indefinite. This motion was carried. Prof. McMurtrie moved that details be left with the chair. Carried.

The following names were then read as applicants for membership :

Dr. C. E. Pellew, New York.  
 Dr. H. J. Wheeler, Kingston, R. I.  
 Dr. J. H. Washburn, Kingston, R. I.  
 Prof. Chas. E. Brewer, Wake Forest College, Wake Forest, N. C.  
 Dr. P. T. Austen, Rutgers College, New Brunswick, N. J.  
 Dr. Edward S. Wood, Harvard Med. School, Cambridge, Mass.  
 Dr. Geo. Archbold, U. S. Navy Yard, Washington, D. C.  
 Dr. Chas. G. Curtman, 3718 N. 9th street, St. Louis, Mo.  
 Dr. Stephen H. Emmens, Emmensite Explosive and Ammunition Co., Emmens, Pa.  
 Major W. R. Livermore, Eng. Corps, U. S. A., Newport, R. I.  
 Chas. A. Pitkin, A. M., Ph. D., Thayer Academy, So. Braintree, Mass.  
 Louis H. Laudy, Ph. D., School of Mines, Columbia College, N. Y.  
 F. E. Thompson, Roger's High School, Newport, R. I.  
 George W. Patterson, Torpedo Station, Newport, R. I.

The reading of papers being in order, the following were presented :

\*" On the Perissad Law."—W. R. Livermore.  
 " On the Relative Intensity of Chemical Force."—L. H. Friedburg.  
 " On Bütschli's Experimental Imitation of Protoplasm."—C. A. Siegfried.  
 \*" Notes on Water Analysis by the Ammonia Method with some new Apparatus."—A. A. Breneman.  
 †" On the Chemical Work of the United States Geological Survey."—F. W. Clarke.  
 †" On Grass Oils."—F. D. Dodge.  
 †" On the Action of the Nitrils on Organic Acids."—C. E. Colby and F. D. Dodge.  
 ‡" On the Influence Method as a Test for Explosives."—C. E. Munroe.

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\*To appear in the October number.

†These papers were merely notes in advance of publications from articles that had already been given to other journals.

‡Withheld temporarily from publication for official purposes.

“ On the Use of the Gooch Crucible as a Silver Voltameter.”  
—Morris Loeb.

“ On the Extraction of Indigotin from Commercial Indigo.”—  
T. A. Morgan.

“ On the Uses of Fluorine for the Softening of Hard Water.”—  
C. A. Doremus.

The meeting was then adjourned.

ALBERT C. HALE, Secretary.



## ON THE DETERMINATION OF THE STRENGTH OF VARIOUS HIGH EXPLOSIVES.

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BY WILLOUGHBY WALKE, LIEUT. 2D U. S. ARTILLERY,  
Instructor in Charge U. S. Artillery School Laboratory.

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This paper was suggested during a series of experiments undertaken some months ago for the purpose of reconciling apparently great inconsistencies with regard to the relative strengths claimed for various newly invented or patented explosives. No originality is claimed for the methods pursued, but it is thought that a summary of the results obtained may prove of value. The great facility with which an explosive can be invented, and the attraction that work of this character possesses for investigators, both great and small, may explain, in a measure, the annual outpour of so called new explosives. Presuming upon the ignorance or lack of scientific knowledge on the part of the practical miner, the most extravagant and misleading claims are made for the majority of these powers, not the least significant of which is that all are equally as strong as, and many of them much more powerful than liquid nitroglycerine. It was in order to verify or disprove this particular claim that the following experiments were undertaken, especially as strenuous efforts have been made by some of the inventors to have their powders adopted for military and naval purposes.

The first step in the work at hand was to provide apparatus for accurately registering the effects of the various explosives, and on account of the limited facilities at my disposal I had little latitude of choice.

Several methods have been devised for the purpose of testing the strength of explosives, but as yet none can be said to give perfect satisfaction. All of them are approximations, nor do the in-

ventors claim more for them. Even the *crusher* used by Berthelot in his elaborate investigations in this direction gave only approximate results, as demonstrated by M. M. Sarau and Vieille.

The majority of the methods pursued seek to determine merely the comparative strength of the explosives, some one explosive being selected as the standard with which all others are compared. It still remains to institute an accurate, absolute scale, by which the strength of explosives may be measured.

After due consideration, it was decided to use the Quinan pressure gauge, both on account of the degree of accuracy with which it registers the pressures developed by the explosives, or rather "by the gases resulting from the decomposition of the explosives," and because of the ease with which the apparatus is manipulated.

The instrument used in the following experiments consists of a heavy block of wood, upon which is bolted a cast iron block or base. In this base are inserted four wrought iron guides or standards, set around the circumference of a four inch circle. A steel plate is let into the iron block flush with its upper surface. A ring holds the guides in place at the top, their ends being reduced to screwbolts passing through the ring, which is held down by nuts.

The piston, which rests upon the plug or cylinder of lead (to be compressed) is a cylinder of tempered steel, four inches in diameter and five inches in length. It is turned away at the sides to lighten it as much as possible. It moves freely between the guides. In the top of the piston is a parabola-shaped cavity to hold the charge of explosive. The weight of the piston is twelve and one-quarter pounds. The shot, made of tempered steel, is four inches in diameter and ten inches in length, weighing thirty-four and one-half pounds. It is bored through its axis to receive a capped fuse.

To operate the instrument, a plug or cylinder of lead is placed upon the steel plate within the guides. The piston is put down gently upon it and the charge of explosive placed in the cavity. The shot is next lowered gently upon the piston and the capped fuse pushed down through the hole in the shot. The fuse being lighted, the charge is exploded when the fire reaches the cap, throwing out the shot and compressing the lead plug. The accu-

racy of the test is based upon the assumption that the lead plugs shall be of uniform density and homogeneous in structure. The form of plug adopted was a cylinder, one inch in diameter and one inch in length. In regard to the kind of plug, the choice lay between plugs cast in molds and plugs cut from a solid bar which could be obtained of the desired dimensions in the factories. This bar, though not made of perfectly pure lead, is manufactured from large masses of metal at a high temperature, is very dense and can be obtained in lengths of fifty feet.

It was decided that the desired uniformity would be more likely to obtain in this product than in plugs cast one at a time from small masses of metal. Having prepared plugs of both kinds, the next point was to test their relative merits for the object in view. The nature of this test was fixed by an additional and independent consideration. It should be borne in mind that, while being compressed by the explosion in the pressure gauge, the density of the plug as well as the lead surface opposed to the piston continually increases.

It is evident, therefore, that the amount of compression shown by the plug is not a direct measure of the strength of the explosive.

For example: if one powder exploded in the pressure gauge compresses a plug  $\frac{2.50}{1000}$ ths of an inch, and another powder compresses a plug  $\frac{5.00}{1000}$ ths of an inch, the latter powder would be twice as strong as the former if the compressions were direct measures of their relative strengths, but from what has preceded, it is evident that the second is much more than twice as strong as the first powder, and the difficulty arises in determining the relation existing between the two.

As a practical measure of the strength, Mr. W. R. Quinan, the inventor of the gauge, to whom I am greatly indebted for valuable information on the subject, assumed that it was proportional to the work performed in reducing the height of the lead cylinder. To get an expression for the work, Mr. Quinan determined, by means of a simple apparatus, the number of foot pounds required to produce the different amounts of compression, and graphically represented the relations existing between the plug compressions and foot pounds by means of a diagram, which was constructed,

using the compressions as the ordinates, and the foot pounds as the abscissas of a curve. The extreme co-ordinates were fixed by nitroglycerine.

As it was impossible to secure one of these diagrams, and as I had not time to undertake the experiments necessary to construct one in time for use for the experiments at hand, it is unnecessary to enter at a greater length into the details of this portion of the subject, especially as the results recorded are referred directly to nitroglycerine as a standard, with no reference to the absolute strengths of the various explosives. While the results registered by the pressure gauge are very reliable as comparative measures for high explosives, they are not equally true and accurate for the lower class. "A triple charge of good black blasting powder, fixed with a fuse, will produce a scarcely perceptible effect on the plug, and yet we know that this powder is capable of great work under certain conditions.

"We may suppose, without an error affecting our principle, that in firing twenty-four grains, or 1.555 grammes, of high powder, the product of the amount of gas, multiplied by the temperature of the gases, gives a number equal to the product of the corresponding elements in the explosion of thrice the charge of black powder. But in one experiment we get a compression which is almost infinitely greater than in the other; for in the last we get a result too small to be measured. It is because the third factor in one formula for explosive effect, *time*, bears a similar but inverse ratio in the two cases: in the first being inconceivably short, and in the second case a sensible interval.

"In the explosion of the black powder, the force, though great, is developed so gradually that at no one instant is sufficient inertia developed in the shot to produce a sensible compression of the lead."

(Report on Vigorit Powder, by Wm. R. Quinan.)

Having decided the means of measurement and secured and tested the lead cylinders, the next step was to select the standard explosive with which to compare all others under examination. It has been shown that the pressure gauge is not an accurate test for the lower explosives, and, as nearly all of the explosives

to be tested belonged to the class of high explosives, nitroglycerine was selected as the standard. The lot of nitroglycerine to be used for this purpose was made some months beforehand, so as to allow it to "clear up" and attain its normal condition, as previous experiments had shown that, during the process of "clearing," nitroglycerine varied in strength from day to day.

The nitroglycerine prepared for use as the standard was very carefully made, the acids and glycerine being tested beforehand, on November 19, 1889, after the method originally pursued at the U. S. Naval Torpedo Station as follows:

$\text{HNO}_3$  (Sp. Gr. 1.50).....1 part.  
 $\text{H}_2\text{SO}_4$  (Sp. Gr. 1.84).....2 parts.

As soon as this acid mixture had cooled

Glycerine (puriss. anhyd.).....1 part

was gradually introduced with constant agitation into

Acid mixture.....6 parts.

Upon total conversion of the glycerine into the nitric ether, the latter was thoroughly freed from all traces of acid, and then poured into a large glass jar, covered with distilled water, and the jar loosely corked.

In about six weeks, the opaque appearance of the oily fluid had entirely disappeared, and it had assumed the normal appearance of pure glycerine. It was carefully tested from time to time and was found to be entirely satisfactory.

The uniformity of the lead cylinders was tested by carefully weighing and testing several taken at random, and all above or below a certain standard, as well as those showing any defects were rejected.

The mean of several weights and measurements gave

Weight of cylinder.....145.729 grm.  
 Length " " .....1".000 2.540 cm.  
 Diameter " " .....1".000 2.540 cm.

In the subsequent work, the difference in weight of the several cylinders did not exceed 10 or 15 mg., while the standard length and diameter of 1".000 2.540 cm. was absolutely maintained.

One other point was determined beforehand, namely, the relative strength of the caps to be used to explode the several charges. This step was deemed advisable lest it should be found necessary to use caps of different strength for the different explosives. The uniform charge of 24 gra., or 1.555 grm. was used in the gauge for all explosives.

## RECORD OF EXPERIMENTS.

I. *Nitroglycerine*, used as the standard of comparison.

Mode of preparation:

HNO<sub>3</sub> (Sp. Gr. 1.50).....1 part.

H<sub>2</sub>SO<sub>4</sub> (Sp. Gr. 1.84).....2 parts.

and of this

Acid Mixture.....6 parts.

Glycerine (puriss. anh.).....1 part.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
	2.540 c. m.		
1	1".000	0".452	0".548
2	1".000	0".450	0".550
3	1".000	0".445	0".555
Mean.....			0".551

II. *Explosive Gelatine*.

Mode of preparation:

Nitroglycerine.....92 parts.

Camphor.....2 parts.

Gun-cotton (soluble).....6 parts.

Note.—The nitroglycerine used in the preparation of this sample of explosive gelatine was made according to the French method pursued at Vonges. Both the nitroglycerine and explosive gelatine were made and tested on the same day.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
4	1".000	0".435	0".565
5	1".000	0".410	0".590
6	1".000	0".399	0".601
Mean.....			0".585

III. *Hellhoffite*.

Mode of preparation:

 $\text{HNO}_3$  (Sp. Gr. 1.50).....53 parts.

Dinitrobenzole.....47 parts.

 $(\text{C}_6\text{H}_4(\text{NO}_2)_2$  added to saturation.)

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
7	1".000	0".415	0".585
8	1".000	0".415	0".585
9	1".000	0".415	0".585
Mean.....			0".585

IV. *Nobel's Smokeless Powder*.

Mode of preparation:

Nitroglycerine..... 50 parts.

Camphor..... 5 parts.

Benzole.....100 parts.

Gun-cotton (soluble)..... 25 parts.

The camphor was dissolved in the nitroglycerine and the benzole added.

Gun-cotton was added and stirred until the whole became gelatinized. The benzole was next evaporated on a water bath, the mass rolled out into a sheet and finally cut up into small cubes.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
10	1".000	0".500	0".500
11	1".000	0".486	0".514
12	1".000	0".485	0".515
Mean.....			0".500

V. *Nitroglycerine*.

Mode of preparation:

According to U. S. Naval Torpedo Station process, and tested immediately upon completion.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
13	1".000	0".491	0".509
14	1".000	0".491	0".509
15	1".000	0".491	0".509
Mean.....			0".509

VI. *Explosive Gelatine.*

Mode of preparation :

Same as in II., Expts. 4, 5 and 6, except that the nitroglycerine was taken from that used in V., Expts. 13, 14 and 15.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
16	1".000	0".520	0".480
17	1".000	0".504	0".496
18	1".000	0".506	0".494
Mean.....			0".490

VII. *Gun-cotton.*

Mode of preparation :

Sample or charge was taken from a disk of U. S. Naval Torpedo Station, Lot No. 100, 1889.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
19	1".000	0".543	0".457
20	1".000	0".543	0".457
21	1".000	0".540	0".460
Mean.....			0".458

VIII. *Gun-cotton.*

Mode of preparation :

Charge taken from a disk of Stowmarket cotton made in 1885.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
22	1".000	0".545	0".455
23	1".000	0".541	0".459
24	1".000	0".541	0".459
Mean.....			0".458

IX. *Nitroglycerine.*

Mode of preparation :

According to the process pursued at Vonges as follows :

The following mixtures were made and allowed to cool :

HNO<sub>3</sub> (Sp. Gr. 1.50).....1 part.

H<sub>2</sub>SO<sub>4</sub> (Sp. Gr. 1.84).....1 part.

and

H<sub>2</sub>SO<sub>4</sub> (Sp. Gr. 1.84).....3.2 parts.

Glycerine (puriss. anhyd.).....1.0 part.



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As soon as cool, 4.2 parts of the sulpho-glycerol was added to 5.6 parts of the acid mixture, the vessel was loosely covered, and the reaction allowed to proceed under a hood for 12 hours.

The nitroglycerine was then separated from the acids and thoroughly washed.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
25	1".000	0".550	0".450
26	1".000	0".548	0".452
27	1".000	0".549	0".451
Mean.....			0".451

### X. Gun-cotton.

Mode of preparation :

This explosive was made in the laboratory according to the U. S. Torpedo Station process, but no effort was made to pulp, poach or press it. It was simply pure trinitrocellulose.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
28	1".000	0".552	0".448
29	1".000	0".552	0".448
30	1".000	0".552	0".448
Mean.....			0".448

### XI. Dynamite No. 1.

Mode of preparation :

Nitroglycerine (same as V.)..... 6 parts.

Kieselguhr..... 2 parts.

Mg CO<sub>3</sub>..... 0.14 parts.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
31	1".000	0".552	0".448
32	1".000	0".552	0".448
33	1".000	0".552	0".448
Mean.....			0".448

### XII. Dynamite de Trauzl.

Mode of preparation :

Nitroglycerine (same as V.)..... 75 parts.

Gun-cotton..... 25 parts.

Charcoal..... 2 parts.

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The gun-cotton and charcoal were very finely divided before being added to the nitroglycerine.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
34	1".000	0".563	0".437
35	1".000	0".563	0".437
36	1".000	0".563	0".437
Mean.....			0".437

XIII. *Emmensite.*

Mode of preparation :

"Emmens Acid" was first made by dissolving commercial picric acid, at a gentle heat, in nitric acid (Sp. Gr. 1.50) and evaporating. The explosive itself was made by fusing together in a paraffin bath

Emmens Acid.....5 parts.

NH<sub>4</sub> (NO<sub>3</sub>).....5 parts.

And then incorporating

Picric Acid.....6 parts.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
37	1".000	0".571	0".429
38	1".000	0".571	0".429
39	1".000	0".571	0".429
Mean.....			0".429

XIV. *Amide Powder.*

Mode of preparation :

KNO<sub>3</sub>.....101 parts.

NH<sub>4</sub> (NO<sub>3</sub>).....80 parts.

Charcoal.....40 parts.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
40	1".000	0".614	0".386
41	1".000.	0".615	0".385
42	1".000	0".616	0".384
Mean.....			0".385

XV. *Oxonite*.

Mode of preparation :

 $\text{HNO}_3$  (Sp. Gr. 1.50).....54 parts.

Picric Acid.....46 parts.

[ $\text{C}_6\text{H}_3\text{O}(\text{NO}_2)_3$  added to saturation.]

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
43	1".000	0".617	0".383
44	1".000	0".617	0".383
45	1".000	0".617	0".383

Mean.....0".383

Note.—In this particular explosive, the picric acid was fused before being added to the  $\text{HNO}_3$ .

XVI. *Tonite*.

Mode of preparation :

Gun-cotton (finely divided).....52.5 parts.

Barium Nitrate.....47.5 parts.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
46	1".000	0".624	0".376
47	1".000	0".624	0".376
48	1".000	0".624	0".376

Mean.....0".376

XVII. *Bellite*.

Mode of preparation :

 $\text{NH}_4(\text{NO}_3)$ .....5 parts.

Metadinitrobenzene.....1 part.

The ammonium nitrate was melted in a paraffin bath, and the  $\text{C}_6\text{H}_4(\text{NO}_2)_2$ , finely pulverized, gradually added and mixed with a wooden spatula until the entire mass became pasty. It was then allowed to cool and was granulated.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
52	1".000	0".638	0".362
53	1".000	0".640	0".360
54	1".000	0".636	0".364

Mean.....0".362

XVIII. *Oxonite*.

Mode of preparation :

Same as in XV., Experiments 43, 44 and 45, except that the picric acid was not fused before being added to the nitric acid.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
49	1".000	0".646	0".354
50	1".000	0".646	0".354
51	1".000	0".646	0".354
Mean.....			0".354

XIX. *Rack-a-Rock*.

Mode of preparation :

KClO<sub>3</sub>.....79 parts.

Mononitrobenzene .....21 parts.

The chlorate was pulverized and saturated with nitro-benzene just before being used.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
55	1".000	0".660	0".340
56	1".000	0".660	0".340
57	1".000	0".660	0".340
Mean.....			0".340

XX. *Atlas Powder*.

Mode of preparation :

Sodium Nitrate.....34 parts.

Sawdust (fine).....14 parts.

Magnesium Carbonate.....2 parts.

Nitroglycerine.....50 parts.

This explosive goes by the trade name of Atlas B.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
58	1".000	0".665	0".335
59	1".000	0".667	0".333
60	1".000	0".669	0".331
Mean.....			0".333

to be tested belonged to the class of high explosives, nitroglycerine was selected as the standard. The lot of nitroglycerine to be used for this purpose was made some months beforehand, so as to allow it to "clear up" and attain its normal condition, as previous experiments had shown that, during the process of "clearing," nitroglycerine varied in strength from day to day.

The nitroglycerine prepared for use as the standard was very carefully made, the acids and glycerine being tested beforehand, on November 19, 1889, after the method originally pursued at the U. S. Naval Torpedo Station as follows:

$\text{HNO}_3$  (Sp. Gr. 1.50).....1 part.  
 $\text{H}_2\text{SO}_4$  (Sp. Gr. 1.84).....2 parts.

As soon as this acid mixture had cooled

Glycerine (puriss. anhyd.).....1 part

was gradually introduced with constant agitation into

Acid mixture.....6 parts.

Upon total conversion of the glycerine into the nitric ether, the latter was thoroughly freed from all traces of acid, and then poured into a large glass jar, covered with distilled water, and the jar loosely corked.

In about six weeks, the opaque appearance of the oily fluid had entirely disappeared, and it had assumed the normal appearance of pure glycerine. It was carefully tested from time to time and was found to be entirely satisfactory.

The uniformity of the lead cylinders was tested by carefully weighing and testing several taken at random, and all above or below a certain standard, as well as those showing any defects were rejected.

The mean of several weights and measurements gave

Weight of cylinder.....145.729 grm.  
 Length " " .....1".000 2.540 cm.  
 Diameter " " .....1".000 2.540 cm.

In the subsequent work, the difference in weight of the several cylinders did not exceed 10 or 15 mg., while the standard length and diameter of 1".000 2.540 cm. was absolutely maintained.

One other point was determined beforehand, namely, the relative strength of the caps to be used to explode the several charges. This step was deemed advisable lest it should be found necessary to use caps of different strength for the different explosives. The uniform charge of 24 gra., or 1.555 grm. was used in the gauge for all explosives.

## RECORD OF EXPERIMENTS.

I. *Nitroglycerine*, used as the standard of comparison.

Mode of preparation:

$\text{HNO}_3$  (Sp. Gr. 1.50).....1 part.

$\text{H}_2\text{SO}_4$  (Sp. Gr. 1.84).....2 parts.

and of this

Acid Mixture.....6 parts.

Glycerine (puriss. anh.).....1 part.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
	2.540 c. m.		
1	1".000	0".452	0".548
2	1".000	0".450	0".550
3	1".000	0".445	0".555
Mean.....			0".551

II. *Explosive Gelatine*.

Mode of preparation:

Nitroglycerine.....92 parts.

Camphor.....2 parts.

Gun-cotton (soluble).....6 parts.

Note.—The nitroglycerine used in the preparation of this sample of explosive gelatine was made according to the French method pursued at Vonges. Both the nitroglycerine and explosive gelatine were made and tested on the same day.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
4	1".000	0".435	0".565
5	1".000	0".410	0".590
6	1".000	0".399	0".601
Mean.....			0".585

III. *Hellhoffite*.

Mode of preparation:

HNO<sub>3</sub> (Sp. Gr. 1.50).....53 parts.

Dinitrobenzole.....47 parts.

(C<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub> added to saturation.)

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
7	1".000	0".415	0".585
8	1".000	0".415	0".585
9	1".000	0".415	0".585
Mean.....			0".585

IV. *Nobel's Smokeless Powder*.

Mode of preparation:

Nitroglycerine..... 50 parts.

Camphor..... 5 parts.

Benzole.....100 parts.

Gun-cotton (soluble)..... 25 parts.

The camphor was dissolved in the nitroglycerine and the benzole added.

Gun-cotton was added and stirred until the whole became gelatinized. The benzole was next evaporated on a water bath, the mass rolled out into a sheet and finally cut up into small cubes.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
10	1".000	0".500	0".500
11	1".000	0".486	0".514
12	1".000	0".485	0".515
Mean.....			0".505

V. *Nitroglycerine*.

Mode of preparation:

According to U. S. Naval Torpedo Station process, and tested immediately upon completion.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
13	1".000	0".491	0".509
14	1".000	0".491	0".509
15	1".000	0".491	0".509
Mean.....			0".509

VI. *Explosive Gelatine.*

Mode of preparation :

Same as in II., Expts. 4, 5 and 6, except that the nitroglycerine was taken from that used in V., Expts. 13, 14 and 15.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
16	1".000	0".520	0".480
17	1".000	0".504	0".496
18	1".000	0".506	0".494
Mean.....			0".490

VII. *Gun-cotton.*

Mode of preparation :

Sample or charge was taken from a disk of U. S. Naval Torpedo Station, Lot No. 100, 1889.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
19	1".000	0".543	0".457
20	1".000	0".543	0".457
21	1".000	0".540	0".460
Mean.....			0".458

VIII. *Gun-cotton.*

Mode of preparation :

Charge taken from a disk of Stowmarket cotton made in 1885.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
22	1".000	0".545	0".455
23	1".000	0".541	0".459
24	1".000	0".541	0".459
Mean.....			0".458

IX. *Nitroglycerine.*

Mode of preparation :

According to the process pursued at Vonges as follows :

The following mixtures were made and allowed to cool :

HNO<sub>3</sub> (Sp. Gr. 1.50).....1 part.

H<sub>2</sub>SO<sub>4</sub> (Sp. Gr. 1.84).....1 part.

and

H<sub>2</sub>SO<sub>4</sub> (Sp. Gr. 1.84).....3.2 parts.

Glycerine (puriss. anhyd.).....1.0 part.



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As soon as cool, 4.2 parts of the sulpho-glycerol was added to 5.6 parts of the acid mixture, the vessel was loosely covered, and the reaction allowed to proceed under a hood for 12 hours.

The nitroglycerine was then separated from the acids and thoroughly washed.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
25	1".000	0".550	0".450
26	1".000	0".548	0".452
27	1".000	0".549	0".451
Mean.....			0".451

### X. Gun-cotton.

Mode of preparation :

This explosive was made in the laboratory according to the U. S. Torpedo Station process, but no effort was made to pulp, poach or press it. It was simply pure trinitrocellulose.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
28	1".000	0".552	0".448
29	1".000	0".552	0".448
30	1".000	0".552	0".448
Mean.....			0".448

### XI. Dynamite No. 1.

Mode of preparation :

Nitroglycerine (same as V.).....6 parts.

Kieselguhr.....2 parts.

Mg CO<sub>3</sub>.....0.14 parts.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
31	1".000	0".552	0".448
32	1".000	0".552	0".448
33	1".000	0".552	0".448
Mean.....			0".448

### XII. Dynamite de Trauzl.

Mode of preparation :

Nitroglycerine (same as V.).....75 parts.

Gun-cotton.....25 parts.

Charcoal.....2 parts.

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The gun-cotton and charcoal were very finely divided before being added to the nitroglycerine.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
34	1".000	0".563	0".437
35	1".000	0".563	0".437
36	1".000	0".563	0".437
Mean.....			0".437

XIII. *Emmensite.*

Mode of preparation :

"Emmens Acid" was first made by dissolving commercial picric acid, at a gentle heat, in nitric acid (Sp. Gr. 1.50) and evaporating. The explosive itself was made by fusing together in a paraffin bath

Emmens Acid.....5 parts.

NH<sub>4</sub> (NO<sub>3</sub>).....5 parts.

And then incorporating

Picric Acid.....6 parts.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
37	1".000	0".571	0".429
38	1".000	0".571	0".429
39	1".000	0".571	0".429
Mean.....			0".429

XIV. *Amide Powder.*

Mode of preparation :

KNO<sub>3</sub>.....101 parts.

NH<sub>4</sub> (NO<sub>3</sub>).....80 parts.

Charcoal.....40 parts.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
40	1".000	0".614	0".386
41	1".000.	0".615	0".385
42	1".000	0".616	0".384
Mean.....			0".385

XV. *Oxonite*.

Mode of preparation :

 $\text{HNO}_3$  (Sp. Gr. 1.50).....54 parts.

Picric Acid.....46 parts.

[ $\text{C}_6\text{H}_3\text{O}(\text{NO}_2)_3$  added to saturation.]

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
43	1".000	0".617	0".383
44	1".000	0".617	0".383
45	1".000	0".617	0".383

Mean.....0".383

Note.—In this particular explosive, the picric acid was fused before being added to the  $\text{HNO}_3$ .

XVI. *Tonite*.

Mode of preparation :

Gun-cotton (finely divided).....52.5 parts.

Barium Nitrate.....47.5 parts.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
46	1".000	0".624	0".376
47	1".000	0".624	0".376
48	1".000	0".624	0".376

Mean.....0".376

XVII. *Bellite*.

Mode of preparation :

 $\text{NH}_4(\text{NO}_3)$ .....5 parts.

Metadinitrobenzene.....1 part.

The ammonium nitrate was melted in a paraffin bath, and the  $\text{C}_6\text{H}_4(\text{NO}_2)_2$ , finely pulverized, gradually added and mixed with a wooden spatula until the entire mass became pasty. It was then allowed to cool and was granulated.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
52	1".000	0".638	0".362
53	1".000	0".640	0".360
54	1".000	0".636	0".364

Mean.....0".362

XVIII. *Oxonite*.

Mode of preparation :

Same as in XV., Experiments 43, 44 and 45, except that the picric acid was not fused before being added to the nitric acid.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
49	1".000	0".646	0".354
50	1".000	0".646	0".354
51	1".000	0".646	0".354
Mean.....			0".354

XIX. *Rack-a-Rock*.

Mode of preparation :

KClO<sub>3</sub>.....79 parts.

Mononitrobenzene .....21 parts.

The chlorate was pulverized and saturated with nitro-benzene just before being used.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
55	1".000	0".660	0".340
56	1".000	0".660	0".340
57	1".000	0".660	0".340
Mean.....			0".340

XX. *Atlas Powder*.

Mode of preparation :

Sodium Nitrate.....34 parts.

Sawdust (fine).....14 parts.

Magnesium Carbonate..... 2 parts.

Nitroglycerine.....50 parts.

This explosive goes by the trade name of Atlas B.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
58	1".000	0".665	0".335
59	1".000	0".667	0".333
60	1".000	0".669	0".331
Mean.....			0".333

XXI. *Ammonia Dynamite.*

Mode of preparation :

Ammonium Nitrate.....	75 parts.
Paraffin.....	4 parts.
Charcoal.....	3 parts.
Nitroglycerine.....	18 parts.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
61	1".000	0".696	0".304
62	1".000	0".696	0".304
63	1".000	0".612	0".388
Mean.....			0".332

XXII. *Volney's Powder, No. 1.*

Mode of preparation :

Nitrated naphthalene No. 1 was first prepared as follows :

Nitro-sulphuric Acid, consisting of

H <sub>2</sub> SO <sub>4</sub> (Sp. Gr. 1.84).....	2 parts,
HNO <sub>3</sub> (Sp. Gr. 1.50).....	1 part,

was made and allowed to cool. Of this

Acid mixture.....	4 parts,
Naphthalene.....	1 part,

were introduced into a vessel and the reaction allowed to proceed for about one hour. The yellow crystalline mass was then thoroughly washed, dried and pulverized.

Volney Powder, No. 1, as made, consisted of

Nitrated Naphthalene, No. 1.....	2.18 parts.
KNO <sub>3</sub> .....	0.19 parts.
Sulphur.....	0.16 parts.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
64	1".000	0".678	0".322
65	1".000	0".675	0".325
66	1".000	0".681	0".319
Mean.....			0".322

XXIII. *Volney's Powder, No. 2.*

Mode of preparation :

Nitrated naphthalene No. 2 was prepared by treating naphthalene with nitric acid as follows :

Naphthalene.....1 part.

 $\text{HNO}_3$  (Sp. Gr. 1.40).....4 parts.

The reaction was allowed to proceed slowly for four or five days, and the brown crystalline mass was then thoroughly washed, dried and pulverized.

Volney's Powder No. 2, as made, consisted of

Nitrated naphthalene No. 2.....1 part.

 $\text{KNO}_3$ .....3.30 parts.

Sulphur.....0.51 parts.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
67	1".000	0".707	0".293
68	1".000	0".707	0".293
69	1".000	0".706	0".294
Mean.....			0".294

XXIV. *Melinite.*

Mode of preparation :

Picric Acid (fused).....70 parts.

Gun-cotton (soluble).....30 parts.

The gun-cotton was dissolved in a mixture of

Ether.....2 parts.

Alcohol.....1 part.

The acid was fused and pulverized, and then thoroughly incorporated in the gun-cotton solution. The ether-alcohol mixture was afterwards evaporated.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
70	1".000	0".718	0".282
71	1".000	0".720	0".280
72	1".000	0".722	0".278
Mean.....			0".280

**XXV. Silver Fulminate.**

Mode of preparation :

Silver (gran.)..... 1 part,  
 was dissolved in  
 HNO<sub>3</sub> (Sp. Gr. 1.308).....20 parts,  
 and the solution thus obtained was poured into a flask containing  
 Alcohol (87%).....27 parts.

Reaction was promoted by bringing this last solution to a temperature of 212° F. As soon as the solution became turbid, it was allowed to cool, and

Alcohol (87%).....27 parts,  
 was again introduced into the flask, and the reaction again started. As soon as all reaction ceased, the opaque, white crystals were thoroughly washed and preserved in a black jar.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
73	1".000	0".723	0".277
74	1".000	0".723	0".277
75	1".000	0".723	0".277
Mean.....			0".277

**XXVI. Mercury Fulminate.**

Mode of preparation :

Same in general as in XXV., except as to proportions as follows :

Mercury..... 10 parts.  
 HNO<sub>3</sub> (Sp. Gr. 1.40).....120 parts.  
 Alcohol (95%).....110 parts.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
76	1".000	0".725	0".275
77	1".000	0".725	0".275
78	1".000	0".725	0".275
Mean.....			0".275

**XXVII. Mortar Powder.**

Dupont's Manufacture.

Number of Experiment.	Length of Cylinder before Compression.	Length of Cylinder after Compression.	Amount of Compression.
79	1".000	0".845	0".155
80	1".000	0".845	0".155
81	1".000	0".845	0".155
Mean.....			0".155

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Assuming then the nitroglycerine made on November 19, 1889, as the standard, and assigning to it, for the purpose of comparison, the value of 100, the results of the foregoing experiments may be conveniently recapitulated in the following table:

Name of Explosive.	Compression of Cylinder.	Order of Strength.
I Explosive Gelatine..... (Made from nitroglycerine after the Vonges Process.)	0".585	106.17
II Hellhoffite.....	0".585	106.17
III Nitroglycerine..... (Made Nov. 19, 1889, tested Jan. 6, 1890.)	0".551	100.00
IV Nobel's Smokeless Powder	0".509	92.38
V Nitroglycerine..... (Made Jan. 29, 1890, and tested on the same day. U. S. N. Torpedo Station Process.)	0".509	92.37
VI Explosive Gelatine..... (Made from the last nitro- glycerine.)	0".490	88.93
VII Gun-cotton..... (U. S. N. Torpedo Station, Lot 100, 1889.)	0".458	83.12
VIII Gun-cotton..... (Stowmarket 1885.)	0".458	83.12
IX Nitroglycerine..... (Made according to the French process and tested on the same day.)	0".451	81.85
X Gun-cotton..... (Made in Artillery School laboratory.)	0".448	81.31
XI Dynamite No. 1.....	0".448	81.31
XII Dynamite de Trauzl.....	0".437	79.31



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Name of Explosive.	Compression of Cylinder.	Order of Strength.
XIII Emmensite.....	0".429	77.86
XIV Amide Powder.....	0".385	69.87
XV Oxonite..... (Picric acid fused before being added.)	0".383	69.51
XVI Tonite.....	0".376	68.24
XVII Bellite.....	0".362	65.70
XVIII Oxonite..... (Picric acid not fused.)	0".354	64.24
XIX Rack-a-Rock.....	0".340	61.71
XX Atlas Powder.....	0".333	60.43
XXI Ammonia Dynamite.....	0".332	60.25
XXII Volney's Powder No. 1...	0".322	58.44
XXIII Volney's Powder No. 2...	0".294	53.18
XXIV Melinite.....	0".280	50.82
XXV Silver Fulminate.....	0".277	50.27
XXVI Mercury Fulminate.....	0".275	49.91
XXVII Mortar Powder..... (Dupont.)	0".155	28.13

While the foregoing table gives correctly the *order of strength* of the various explosives contained in it, it cannot be said to give their actual *relative strengths*, since it was, for reasons given, impossible to arrive at their absolute strengths expressed in any unit of force. The true relations existing between them would be expressed by the relative amounts of work required to compress

the cylinders to the lengths shown in the second column, and, as already shown, the greater the amount of compression, so much greater the ratio for each additional 1-1000th of an inch of compression. From the results recorded in the above table, we may conclude that whatever other claims may be advanced for the various explosives tested, that with regard to their strength as compared with nitroglycerine is misleading. Under certain conditions, readily understood, some of these new inventions are capable of accomplishing more work than pure nitroglycerine, and as the performance of mechanical work may also be considered a measure of strength, it would at first sight appear that such claims are in so far sustained. But in by far the majority of such cases the additional strength is derived from the physical condition of the explosive rather than from any inherent property of the active principle. Let us look into this briefly.

Prof. C. E. Munroe, chemist to the U. S. Naval Torpedo Corps, in a hasty review of a "Report upon Experiments and Investigations to develop a System of Submarine Mines for defending the Harbors of the United States," submitted to the War Department by General Henry L. Abbot, Eng. Corps, U. S. A., says :

"In comparing the results obtained for pure nitroglycerine with those for Dynamite No. 1, there was revealed what at first sight appears to be a paradox.

"One pound of pure nitroglycerine was found to exert only 81 per cent. of the intensity of action of three-fourths of a pound absorbed by an inert substance which could add nothing to the heat or gases developed.

"This fact, which was discovered early in the trials, was considered so extraordinary as to require careful verification and study.

"The first explanation suggested was that it was due to a possible variation in the strength of the nitroglycerine itself depending upon a difference in the chemical composition of different samples.

"This was tested practically with different nitroglycerines, and with nitroglycerine and dynamite made from it, and it was shown, beyond question, that variations in the quality of the nitroglycerine

had nothing to do with it, and that the explanation must be sought in the physical conditions of the problems.

“General Abbot, therefore, suggests that in granulating nitroglycerine, by absorbing it in kieselguhr, the particles of silica slightly retard chemical action—since, in detonations, the reactions occur within the molecules—and as the resistance opposed by water is of a slightly yielding character, more time may be required to reach this condition than is afforded by nitroglycerine, pure and simple.

“This view is confirmed by the action of certain dynamites which are made so as to explode with exceeding rapidity, and which fall very low in the scale.”

(Notes on the Literature of Explosives, by Prof. C. E. Munroe, B. S., May, 1883.)

This explanation is given as applying to the most extreme case in which nitroglycerine is the active principle in both explosives, the inert absorbent in the case of dynamite in no way contributing to its strength. Subjecting the explosives contained in the above table to a further test of strength by a comparison of the actual performance of mechanical work by proportional charges of each taken from the third column of the same table, the results of the previous experiments were fully verified.

## THE VOLUMETRIC COMPOSITION OF WATER.

BY PROF. E. W. MORLEY.

(*Abstract.*)

Gay-Lussac and Humboldt made ten experiments on the volumetric composition of water, with a mean error of  $\frac{1}{216}$ . Scott made at least twenty-five experiments, but without reducing the mean error.

The author was engaged in the same determination before Scott's papers appeared. After much labor he was able to procure hydrogen in which no impurity was present except nitrogen; he constructed an apparatus by which it was possible to detect and measure this residual impurity with a mean error less than  $\frac{1}{100000}$ ; and finally he obtained hydrogen in which no nitrogen could be detected. Oxygen, by use of a similar apparatus, could be examined as rigorously; and finally was obtained with no impurity amounting to  $\frac{1}{100000}$ .

With gases containing no impurity, or containing only a known amount of a known impurity, twenty experiments have been made on the volumetric composition of water, besides four experiments which were lost, two by oxidation of mercury in the eudiometer, and two by accident to the apparatus during an experiment. Of these twenty results, the maximum was 2.00047; the minimum, 2.00005; and the mean, 2.00023. The mean pressure at which the measurements were made was 71 c.m. If, then, oxygen and hydrogen be measured at about the atmospheric pressure, the ratio in which they combine differs from an integral ratio by about one nine-thousandth part. The mean error of a determination was  $\frac{1}{28000}$ .

## CARBON AN IMPURITY IN HYDROGEN AFFECTING DETERMINATION OF ATOMIC WEIGHT.

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BY PROF. E. W. MORLEY.

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### *(Abstract.)*

It is very difficult to obtain hydrogen free from carbon, if zinc is employed.

1. If zinc be dissolved in dilute acids, carbon contaminates the escaping hydrogen. No sample of zinc yet obtained by the writer gave hydrogen in which carbon was not quickly shown by passing it over heated copper oxide and into lime water.

2. If zinc be amalgamated, put into dilute acid and hydrogen obtained electrolytically, it still contains carbon, which has been proved in the same way.

3. If the purest zinc obtainable in commerce is heated in a vacuum, it gives off a gas containing carbon not in the form of the dioxide. Dr. William H. Burton kindly made many experiments on this matter: sixty grammes of zinc gave sometimes 0.8 c.c. carbon dioxide by combustion of carbon existing in the gas given off on fusion in some form other than carbon dioxide. All samples also gave off nitrogen.

4. It is obvious that metallic aluminium is likely to contain gases imprisoned in it and derived from metallurgical processes.

5. The electrolysis of an alkaline hydroxide is likely to give an impure hydrogen unless alkaline carbonates be removed. Such electrolysis, where a carbonate had been purposely added, in a voltameter most thoroughly cleaned from all organic matter, gave hydrogen containing a notable amount of carbon.

The bearing of these facts on the determination of the atomic weight of hydrogen is obvious.

## A NEW FORM OF AIR THERMOMETER FOR TECHNICAL PURPOSES.

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A comparison of several ordinary thermometers in use in a varnish factory showed, as was anticipated, considerable differences in reading under similar circumstances, these differences amounting to as much as  $50^{\circ}$  F. at a temperature of  $500^{\circ}$  F. or thereabout. A part of these differences could be ascribed to age, one of the instruments being about fifteen years old; but only a small part of the differences were due to any such cause. Inquiry of parties who make a business of correcting thermometers disclosed the fact that very little had been done in the way of correcting thermometers for high temperatures, and the conclusions finally reached were as follows:

It appears to be customary to assume the expansion of mercury to be uniform; but this is said not to be the case when we approach its boiling point, and I have not found any statement as to its expansion at high temperatures under pressure, as in the nitrogen-filled instruments.

It is customary to assume the expansion of glass to be uniform; but this is not true when we approach the softening point, and in any given instrument it is impossible to tell how much of an error is thus occasioned.

In graduating a thermometer it is customary to assume that all that part of the instrument which at the time is full of mercury is immersed in the fluid which is under examination; and the error from this cause is stated by an expert to be probably as much as  $80^{\circ}$  F. at temperatures approaching the boiling point of mercury.

The improved method for graduating instruments for use at high temperature appears to be by the use of substances of high

boiling point, such as naphthaline and benzophenone. But different observers find different boiling points, even for a simple substance like mercury, and to get even approximate accuracy the experimenter would be obliged to determine with an air thermometer the boiling point of each substance he used, under the conditions of use.

Finally, the conclusion appears to be inevitable that the thermometer must be standardized under conditions essentially or absolutely similar to those under which it is to be used.

The conditions in the particular case in which I am interested are as follows: The thermometer tube is about three feet long, the graduation being confined to the upper one-third, and is inclosed in a tubular case, which terminates at the bottom in a steel cylinder which surrounds the bulb and is partly filled with mercury. This instrument is put in a copper kettle about two feet deep and has about a foot of the lower part of the instrument immersed in hot oil. Now any reading based on the ordinary graduation will under these circumstances be so erroneous as to be of no absolute value, and in fact, varnish makers do not go by degrees, but put arbitrary marks on their instruments and heat up to the mark, these marks not being at the same scale points of different thermometers.

I desired to make a thermometer which would give a reading within 5° F. of absolute accuracy, and the means I employ are as follows :

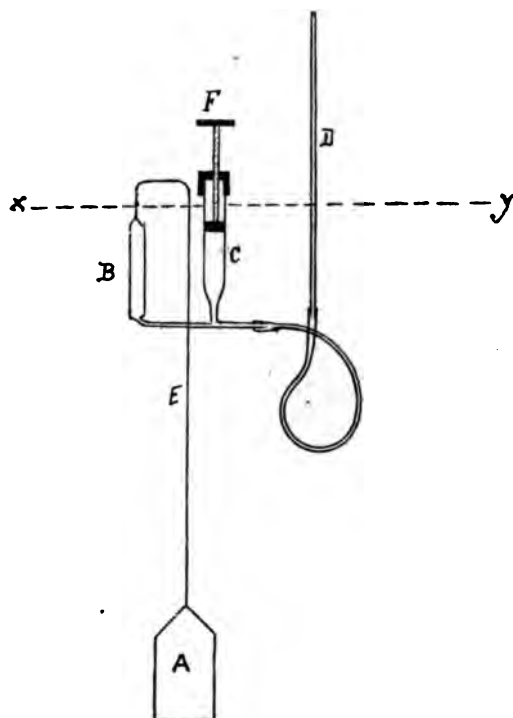


Fig. 1.

## DESCRIPTION OF THE DIAGRAM.

- A.....Bulb.  
 B.....Safety chamber for air and mercury.  
 C.....Mercury cylinder.  
 D.....Air pressure gauge.  
 E.....Capillary tube.  
 F.....Piston with screw to force mercury from C.  
 x y...Horizontal line showing level of mercury in capillary tube  
           and gauge glass.

To avoid the irregular expansion of glass heated to near its softening point I use a bulb of metal, iron being selected; all the experiments which have been made tend to show that the rate of



expansion of iron at temperatures not exceeding 800° F. is very uniform, and on general principles we should expect this to be the case, since such temperatures are far from its softening point. A bulb of cast iron containing about 160 c.c. is fitted by an asbestos-packed joint to a capillary glass tube; the capacity of the bulb is of no consequence except that it should be large enough to make the capacity of the capillary tube insignificant. This glass tube is of any convenient length, say 3½ feet, and after bending downward is connected with a chamber to prevent the escape of air, as shown in the accompanying diagram. This safety chamber is normally filled with mercury, which is forced into it by a piston which is screwed into a cylinder filled with mercury which communicates with this safety chamber, and by this means the thermometer is made a constant volume one. This mercury also connects with a suitable pressure gauge; the form which I use is a closed tube containing air which is connected by a rubber tube with the safety chamber. Owing to the flexibility of the connection the gauge tube can always be placed so that the mercury in it shall be at the level of the mercury in the capillary tube and thus any correction on that account is avoided, and the whole apparatus being closed no correction for barometric pressure is needed. Of course an open mercury gauge tube could be used just as well if desired. What occurs when the bulb is heated is this: The expansion of the air is exactly counterbalanced by the operator who screws down the piston of the mercury cylinder so as to keep the mercury at the same point in the capillary tube; the only effect then of the heat is to increase the pressure on the mercury. The mercury transmits the pressure to the air in the gauge glass, which is compressed, and from the amount of this compression the temperature is calculated.

The calculation was made in the following manner: The expansion of air is  $\frac{1}{273}$  of its 0° C. volume for each degree C. it is heated; or  $\frac{1}{491.4}$  its 32° F. volume for each degree F. it is heated.  $\frac{1}{491.4} = .002035$ , and 1 volume air at 32° F. becomes 1.07733 vol. at 70° F. Since 70° F. is the lowest ordinary temperature in the places

where I am likely to use this instrument, for reasons which are obvious, I have selected 70° F. as my normal temperature. Other observers of course would calculate other tables. Now if we assume 70° F. as normal, what will be the expansion of a given volume of air? The given volume will fill the space which would be occupied by 1.07733 volumes if the temperature were 32° and therefore consists of  $\frac{100000}{107733} = .9282$  of the amount of 32° air which it would take to fill the space; and as its expansion is calculated on 32° air, it will expand .9282 of .002035 = .00188 . . . of its own 70° F. volume for each degree F. it is raised in temperature.

If air at 70° tends to expand .00188 . . . of its volume when heated 1° and is prevented from doing so by being enclosed in a rigid vessel, the pressure is equivalent to that produced by pumping in .001888 of the original volume and keeping the temperature at 70°. In that case we should have 1.001888 vol. condensed to 1.0000 vol.; and the original 1 volume would be condensed to .998113 as found by the proportion 1.001888 : 1 :: 1 : .998113; and so on. Thus a rise of 10° F., that is, to 80° F., would produce a condensation found by this proportion : 1.01888 : 1 :: 1 : .9814 and the space occupied by the condensing agent, which is the mercury in the gauge glass, is .0186 of the normal volume of the gauge, for *this* interval of 10° F. To get the volume at each successive interval of 10° F., multiply .0188 . . . by one, two, three, and so on, and add the product to unity for the first member of the proportion, whence we get a table, which does not, however, allow for the expansion of the iron bulb, nor for a change of temperature in the air of the gauge glass.

The cubical expansion of cast iron is .0000336 for 1° C. If the shell be heated to 800° F., from 70° F., which is equal to 405.6° C., it will expand  $.0000336 \times 405.6 = .01363$  of the original volume of the bulb. At 800° F. the volume of the air in the gauge is .4203 of its normal volume; and  $.4203 \times .01363 = .00573$ , this latter fraction being the part of the normal volume of the gauge which the air in it will expand on account of the increase of the size of the iron bulb at 800° F. This makes a difference in reading such

as would be caused by a difference of about  $16.8^{\circ}$  in temperature. Actually the volume of the air in the gauge is  $.4203 + .00573 = .42603$  of its normal volume, when the bulb is heated to  $800^{\circ}$  F.

In this manner a corrected table may be derived from the table already calculated, and this corrected table will show the absolute temperature of the air in the bulb, when the air in the gauge glass is at  $70^{\circ}$  F.

At  $200^{\circ}$  F. the volume of the air in the gauge glass if at  $70^{\circ}$ , is .8047 of its normal volume. Now if the original volume were raised to  $80^{\circ}$  F. it would have the volume 1.01888, and if this volume were subjected to sufficient pressure to compress it to .8047 of its bulk it would occupy  $.8047 \times 1.01888 = .8762$ . This exceeds the  $70^{\circ}$  volume by .0715, since  $.8762 - .8047 = .0715$ ; and the difference for  $10^{\circ}$  in the bulb at this temperature ( $200^{\circ}$  F.) is

.0119; and  $\frac{.0715}{.0119} = 6.01$ ; hence an elevation of  $10^{\circ}$  in the gauge air temperature makes a difference of  $10 \times 6.01 = 60.1^{\circ}$  in the reading and this amount should be added to the observed temperature under such conditions; and this ratio of 6.01 : 1 is true not only of the temperature of ten degrees in excess of  $70^{\circ}$  in the gauge glass, but also of all temperatures in excess of  $70^{\circ}$  when the bulb temperature is  $200^{\circ}$  F. In this way a table of corrections may be calculated for the various bulb temperatures to be observed. The ratio increases as the temperature rises. The air gauge of the instrument should contain a small thermometer, and a sliding scale can be arranged if desired.

## A RAPID AND EASY METHOD OF ESTIMATING UREA IN URINE.

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By E. H. BARTLEY, M. D.

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This apparatus was designed for the use of physicians rather than chemists. The process is a modification of the well known hypobromite process, by which the urea is decomposed, with the formation of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and free nitrogen. The first two of these remain in solution, while the nitrogen escapes and is measured.

The hypobromite solution is usually prepared by dissolving 25 c.c. of bromine and 100 grms. of sodium hydroxide in 250 c.c. of water. To avoid this tedious and disagreeable preparation I prepare the solution as needed by mixing, in the apparatus, a 20% solution of potassium bromide and sodium hypochlorite (Labaraque's solution), in the proportion of one of the former to about three of the latter.

The result of this mixture is a solution of sodium hypobromite and potassium chloride, answering in every way the requirements of the process.

The two solutions keep well, while the hypobromite solution does not.

The apparatus consists of two parts: First—A graduated pipette delivering 1 c.c. Second—A graduated tube about 1 cm. in diameter and 30 cm. long, closed at one end, and graduated from this closed end throughout its entire length. The graduation is made as follows: A standard solution of urea is prepared containing 10 grains to the fluid ounce. With an ordinary gas tube it was found that 1 c.c. of this solution gave 8.2 c.c. of nitrogen.

This is about the average urea strength of normal urine. Each 8.2 c.c. on the new tube are then divided into ten principal divisions, and each of these into four smaller divisions.

Each of the principal divisions then represents grains per fluid ounce, when 1 c.c. of the urine is taken.

By a similar method the graduation may be made to represent grams per litre.

The process is conducted as follows:

Holding the ureometer in the left hand pour in enough of the 20 per cent. solution of potassium bromide to fill it to the fifth division; then add hypochlorite solution to the eighteenth or twentieth mark. The tube is now inclined and water added to about the twenty-fifth division. With the small pipette 1 c.c. of urine is now added, allowing it to run down the side of the tube so that it shall mix with the water floating upon the heavier solution below. The open end of the ureometer is now firmly closed with the thumb, and its contents thoroughly mixed by inverting it a few times. When the effervescence ceases, which usually takes about two or three minutes, invert and read off the height of the liquid in the tube.

The thumb is now removed under water, the tube depressed to bring the liquid in the tube to a level with the water in the outer vessel, and a second reading taken. The difference between the two readings gives at once the number of grains of urea in each fluid ounce, or grammes per litre, according to the construction of the scale.

This number multiplied by the number of ounces passed in twenty-four hours, in the one case, or litres in the other, gives the amount of urea passed in twenty-four hours, which should be about 500 grains, or 30 to 33 grms. The instrument may be had of Eimer & Amend.

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NOTE.—Experiments made to determine whether the apparatus could be used to determine total nitrogen, after decomposition in the Kjeldahl flask with sulphuric acid, gave good results.

Experiments with ammonium chloride showed that but one-third of the nitrogen was set free from this salt, while the sulphate seems to yield all of its nitrogen.

## STUDIES UPON RESINS.

BY L. H. FRIEDBURG, PH. D.

Resins have, at different times, been subjected to chemical treatment and as far as some of them are concerned, we have quite valuable knowledge of the same. We know of abietinic acid in rosin, we know of a peculiar facility of reaction between some of them with phenol, but still, if asked, what is a resin, chemically speaking, cannot give an explanation.

### I.—COPAL RESIN.

I have begun to study, qualitatively, a resin of great practical importance in the manufacture of varnishes, the so called copal. The difficulty which meets us at the outset of such researches is this: Are we always sure of finding the same raw material under such a name, for example, as copal? What is copal, not chemically but commercially?

We find soft copals, such as damar, which is soluble in ether, but there are other half hard, and still other perfectly hard copals which only partially dissolve in different solvents, but which can be made soluble by allowing them to suffer previously a chemical change. After this, however, we have no longer to do with the raw product "copal," but with a product of decomposition of the same. The soft copals are said to be found mainly on the islands of Sumatra, Java, Molucca and the Philippines, also in Australia. The hard copals are imported via Calcutta and Bombay from some places in Africa. All of these have very different appearance and different physical properties, so different that it seems almost impossible to attribute the same name to them. Their origin is not very clear. The hard copal is called hard animi in England; it is imported into Europe via Calcutta and brought there by African

traders from Zanzibar and the adjoining coasts. The hard copal from Bombay is brought to that place from Madagascar. It is found in Madagascar, Mauritius, Bourbon and is said to be furnished by a tree *Hymenaea Verrucosa*. (Jussieu calls it *Taurouyon*). On l'Ile de France the tree is called *copallier*. We learn also that *Hymenaea Courbaril* of Cayenne furnishes a substance similar to hard copal. (Henry Violette, *Fabrication des Vernis*, p. 302 to 304).

Now, the fact of a vegetable origin of copal seems to be evident. But the growers mix pell mell, soft and hard copals, with other resins and ship them as hard copal. The dealers assort these mixtures and the manufacturers of varnish must rely upon them as well as upon their own knowledge in buying a uniform article. So much as to the origin of copal. The chemical properties of hard copal, as far as the varnish manufacturers are interested in them, are the following: it is insoluble as a whole in alcohol, ether, and oil of turpentine, but becomes soluble in these latter two when previously heated.

Since most hard copal varnishes are solutions in oil of turpentine and linseed oil, we have to remember how the manufacturers proceed. They heat the copal until it melts and continue this heating according to routine. At the same time oil of turpentine is heated to boiling, and at a certain stage of this manipulation the two hot liquids are mixed together in certain proportions. If the copal is not hot enough, and if the hot oil of turpentine is not allowed to run slowly into the former, a clear solution is not obtained. That a great manufacture (dangerous also, as far as inflammability and irritating exhalations are concerned), rests thus upon a most empirical basis is surely the reason for the issue of innumerable patents in regard to changes in the same, changes which, however, have not generally been adopted. (See Ure's Dictionary, 7th Ed., p. 1055.)

But the chemist may approach this task in a different way. He arrives at the knowledge of the real composition of a compound or a mixture through the study of products of decomposition of the same. The synthesis of indigo was only effected after a most perfect study of its products of decomposition had been made.

We know from the above that copal suffers decomposition by heat in such a manner as to leave a residue soluble in boiling oil of turpentine to a varnish. Consequently the exact conditions of this decomposition should be ascertained. Heating copal slowly in a flask connected with a Liebig's condenser, a light flowing distillate which has an agreeable odor, suggestive of terpenes, even of lemon, passes over at first. This odor indicates the presence of the *limonen*, of Wallach. (*Ann. Chem., Liebig*, 252, 108.) Shortly after this, vapors arise which cannot be condensed and which are of an irritating nature, the mass turns darker brown, and the boiling continues in this way until almost all of the copal is destroyed. Performing this experiment with the aid of a thermometer in a fraction flask, we see the aromatic oil distil at temperatures above 100° C. up to 170° C. or 185° C. \* The mass boils quietly, then the white vapors, which partially condense to a liquid of empyreumatic odor, begin to appear when the temperature of 215° C. is reached, the mass turns very dark, boils quietly without sending off visible vapors and the thermometer *falls* suddenly and rapidly to 170° C., or even below that temperature. It seems to follow from this, that while up to 215° a fractional separation of a mixture is going on, when this temperature is reached the heat applied is partly used for more profound inner decomposition of the residue in the flask. If, therefore, the copal be only heated to 182° C. until no more distillate is obtained, and then allowed to cool, we avoid this latter decomposition.

Copal thus heated to 182° C., when allowed to cool, yields a very brilliant glass-hard, translucent resin, which is soluble with the greatest facility in cold or warm oil of turpentine.

The distillate obtained forms  $\frac{1}{3}$  of weight of the raw copal used.

In order to obtain the first volatile oil of agreeable odor in purer

\* In all the data given in this paper in regard to temperatures, the thermometer is always supposed to be in the *vapor* above the liquid and never immersed *in* the liquid. In a subsequent paper experiments will be reported which I have made with a view to determine both temperatures simultaneously, those of the melted gum as well as of the vapors formed.



form, distillation in a current of steam was resorted to. The oil obtained floated on water, but was not obtained in quantities sufficiently large.

The experiment was repeated on a larger scale (with the liberal aid of Dr. Alsberg and in his factory) in a copper still and with 45 pounds of steam pressure.\*

Then again the cooler was not adequate to allow full condensation, and the room was filled with an agreeable odor suggestive of lemon terpenes. The residue in the still, when cold, was very hard, but porous and consequently brittle. It did not dissolve in oil of turpentine.

Next it was ascertained what liquids would dissolve copal without previous treatment. It is said that the distillate obtained from copal by destructive distillation is a solvent for melted copal. But the evil odor makes this unmanageable. It was proved to be correct, as found by former investigators, that aniline and its homologues dissolved copal very readily.

Nitrobenzol or chloroform dissolved copal, the former better than the latter, which, like almost all commercial chloroform was not free from an inflammable admixture, perhaps undecomposed acetone.

Phenol dissolves copal well. This is a known and patented fact. I found cyneol to be an extremely good solvent for copal. (For Cyneol, see *Ann. Chem. Liebig*, 225, 295.)

An astonishing reaction took place when copal was treated with benzaldehyde. This latter dissolves in a most perfect manner at first. Shortly afterwards the whole mass thickens to a light amber colored jelly, not unlike new peach gum, only much softer. It is almost impossible to handle this mass. After some experience it is possible to bring it into a flask and to subject it to distillation. Better results are obtained when ground copal is put into a flask and the  $C_6H_5COH$  added. A perfectly clear solution is obtained. At 80° C. the jelly form is reached, and care has to be taken that continued heating does not crack the flask.

\*I also owe to Dr. Alsberg's kindness a liberal supply of a most uniform, rather pale copal (Kauri gum), of a quality superior to that ordinarily used for varnishes.

Then thick yellowish white fumes are driven through the cooler and  $C_6H_5COH$  and some  $H_2O$  distil off. Later an oil which irritates the eyes follows. Finally an oil distils which condenses to thick white crystals either in the condensing tube or according to temperatures in the receiver. This crystalline mass is soluble in ether and also in benzaldehyde. When this experiment was performed after prolonged treatment of copal with benzaldehyde, under an upright condenser, the result was similar. On distilling, the temperature must not rise above  $215^{\circ}C.$  or more profound decomposition takes place.

A peculiar fact connected with this experiment was that an increase in weight of 8% was noticed, when the quantity of products obtained was compared with the quantity used. This is suggestive of oxidation through atmospheric oxygen, as far as the distillate is concerned. These experiments will be followed up closely and reported upon later.

Resuming the study of solvents for crude copal, oil of turpentine was inverted at  $+270^{\circ}$  and seemed to be a solvent. Glacial acetic acid dissolved copal partially. Carbon disulphide is taken up by copal in large quantities, copal being a colloid with the former. On adding more disulphide the plastic mass rises to the surface and on filtering and drying becomes brittle. The solution of  $CS_2$  was evaporated on a water bath and furnished a gummy, light yellow colored mass of aromatic odor. The plastic mass when exposed to air resumes a hard and brittle form. Copal heated together with glycerine without pressure does not form a fatty substance. The experiment in pressure tubes has not yet been performed.

When conc.  $H_2SO_4$  acts upon copal, sulphur dioxide is generated and the mass turns dark brown.

Chromic acid, even boiling, does *not* act upon copal.

When the oxidizing mixture of potassium dichromate and  $H_2SO_4$  is used a strong action takes place and an odor suggestive of that of the dried leaves of *Asperula Odorata* is noticed.

Strong sodium hydrate of  $40^{\circ}Be.$  does not act appreciably.

Potassium permanganate attacks copal on boiling.

When boiled with nitrosylsulphuric acid, a reaction, which is

not violent takes place. It appears that a nitro product is formed. The product of reaction when poured into water separates yellow flocks which dissolve in alkalies with mahogany color.

Sulphur introduced into boiling copal develops hydrogen sulphide. The mass turns very hard and black, and becomes unmanageable. For instance, it is not easily attacked by alkaline solutions.

A very strong reaction takes place when reducing substances are brought together with copal. Alcoholic ammonia acts strongly when warm. The alcoholic solution deposits besides sulphur, a *white* solid compound when neutralized by acids. The residue that did not dissolve in alcohol when boiled with water puffs up to a very porous mass, not unlike beaten white of egg. This mass when dried is easily crushed to a fine powder which is entirely volatile when gently heated.

Watery ammonium sulphide, reacts on boiling, upon copal. The warm solution is blood red but on cooling becomes lighter colored. The residue after boiling with water and treating with dilute  $H_2SO_4$ , develops lemon odor.

Watery ammonium hydrate was used in order to see whether an abietinic acid salt might be obtained. The product of the reaction turns at once snow white: it does not float upon the liquid but sinks in it as a heavy white powder. Also this ammonium salt volatilizes entirely, without leaving a residue.

Solid potassium cyanide fused with copal developed very bad odors and was abandoned.

The reaction of grape sugar in alkaline solution is an exceedingly lively and sudden one, which could not be tempered.

Also alcoholic potassium reacts with copal when moderate heat is applied.

Strong hydrochloric acid attacks copal slightly.

Zinc dust heated with copal develops currents of hydrocarbons, some of which do not condense, while iron powder is without action. Zn and  $HCl$  do not show any reaction.

The experiments performed so far are those of destructive distillation, of oxidation and reduction as stated above. Furthermore, the remarkable reaction with aldehydes, such as benzalde-

hyde and that with nitrosylsulphuric acid to form nitro products and the formation of an ammonium salt which is as volatile as ammonium chloride.

All these experiments will next be performed quantitatively, and should then allow definite conclusions in regard to my assumption that the crude copal consists of three typical components, a terpene, an easily oxidizable hydrocarbon not a terpene, and an acid which may be homologous with abietinic acid. This acid has the peculiarity of being an amorphous, glass-hard and translucent mass.

NEWPORT, R. I., Aug. 6th, 1890.

## ON THE RELATIVE INTENSITY OF CHEMICAL FORCE.

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BY L. H. FRIEDBURG, PH. D.

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We are accustomed in chemistry to use the words "chemical attraction," or "affinity," without forming a distinct conception as to the manner in which this affinity may act.

The different degrees of readiness with which elements combine suggests the question: What is the cause of this difference in behavior? Some chemical compounds are less stable than others. Even the elements in their pure molecular state are split with greater facility in some cases than others into atoms before entering into new compounds. We are accustomed in this latter case to speak of a resistance which the molecule of an element offers before it enters into combination with other elements. We note that there is a force acting between the atoms of the same element and between those of different elements. We call this the chemical force.

Amongst the newer stereochemical conceptions there is one, expressed by Alex. Naumann\* in the following words:

"The greatest possible effect of the attractive force between carbon atoms takes place when the directions of attraction coincide with the line which unites the centres of gravity of two such atoms. If the directions of attraction deviate from this line, only that component of the total attraction links the atoms, which lies in the direction of this line." If this be true, it follows naturally that even two carbon atoms may be held in combination by a greater chemical force than that which holds two other carbon atoms together. The reason is to be found in a different stereochemical arrangement.

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\* Ber. d. Chem. Ges., 23, 477, 1890.

In applying this idea to the chemical force in general, we find that this force is dependent upon the direction in which it is exerted. Older speculations, notably those of Berthollet, have impressed upon us the idea that the atomic weights have an influence upon this force, although not in such a general sense as Berthollet assumed it. We must add to this the principle of valency, which tell us that the atoms of some elements offer one point of attack to the chemical force while others offer two, three or four points of attack.

Thus we consider chemical force to be dependent upon atomic weight, valency and the direction in which this force acts between the atoms. From this standpoint we may explain chemical action with greater clearness than the mere use of the words affinity or chemical attraction admit of. For example, we find in the first place, that some elements are more ready to display chemical force than others. A hydrogen molecule is more easily split into atoms than a nitrogen molecule. We notice here that for a molecule of an element there is no difference of weight to be noticed, since these molecules are supposed to consist of two or more atoms of the same weight. But the difference of valency and of the direction of the action of force between such molecules need not be the exclusive cause of such difference in behavior as is displayed by hydrogen and nitrogen. The univalent hydrogen atom is bound by a chemical force acting in a straight line to another atom of hydrogen exactly equal to the first; this line evidently has the direction of the line which unites the centres of gravity of the two atoms. We purposely neglect here the theory of rotation of such a system. Two triatomic nitrogen atoms, forming a molecule, are supposed to represent the figure of a three sided double pyramid, the nitrogen atoms occupying two opposite corners.\* The direction of any of these valencies which are supposed to act along the edges of the pyramids, certainly do not coincide with the line uniting the centres of gravity of the two atoms. We surmise, therefore, that although one single valency of the triatomic nitrogen atom is equivalent to one hydrogen valency, that the strength of chemical action within the nitrogen molecule cannot be exactly three times

\* Ber. d. Chem. Ges., 23, 11, 1890.

as large as within the hydrogen molecule, but that it must be smaller to some extent.

It has been suggested above that the atomic weight might, in some way, come into consideration even when molecules of the elements were conceived of. If the chemical force is supposed to be the result of the vibrating ether coming into contact with elementary atoms, it is clear that this force will more easily join together the lighter atoms than the heavier, that consequently the heavier atoms are kept together by an absolutely stronger pressure. If we add that this force finds three points of attack in the nitrogen atom, and but one in the hydrogen atom, we see the possibility of the nitrogen molecule being less ready to display chemical force towards molecules of other elements than the hydrogen molecule.

We may extend this example to the *different* mono-, di-, tri- and tetratomic elements. We shall find, however, that oxygen and sulphur, for example, although both diatomic in *certain* compounds, show a difference in regard to readiness of combining with other elements. The influence of the atomic weight being perceptible in the above sense. Of course, we must allow for the different states of aggregation. Solid sulphur will be slower to react than gaseous oxygen; but we may consider both at the same temperatures in gaseous form, and thus eliminate this influence. As an example, we shall find that carbon dioxide is easier to prepare synthetically than carbon disulphide, water than hydrogen sulphide.

Concerning the *stability* of a chemical compound *formed* from atoms of different elements we find several cases possible.

Firstly, such compounds are more or less stable at ordinary conditions, and without being acted upon by other chemical elements or compounds. This is illustrated by ammonia gas and nitrogen chloride.

The hydrogen atom being fourteen times lighter than the nitrogen atom, it will not be able to bend the valency of nitrogen from its original direction, and the three hydrogen atoms may be considered as symmetrically arranged with reference to the nitrogen. The chlorine atom being two and a half times heavier than

nitrogen, the three chlorine atoms representing a weight seven and a half times that of the nitrogen atom, may influence the directions of valency of this latter.

A compound is thus formed (assuming for brevity's sake that its formula be  $\text{NCl}_3$ ) which gives us the conception that chlorine atoms in this case are more nearly in reach of and more likely to act upon one another to form chlorine molecules, and that nitrogen has a tendency in its valencies to spread out to their original direction, forming a nitrogen molecule with a similarly moving nitrogen atom. The whole compound is thus in a state of unstable equilibrium which is easily disturbed with the well known results. In *this particular case* it is difficult to decide whether the atomic weight of chlorine contributes more to the production of an explosion than the tendency of the curbed nitrogen valencies to spread back and to form an original nitrogen molecule. For the other explosive nitrogen compounds the case is a little more complicated, but it follows by analogy that the cause of the decomposition should not be ascribed to the above mentioned peculiarity of nitrogen alone. In all the explosives which contain *nitro* groups (potassium nitrate of gunpowder *not* excluded), it is just as much the tendency of oxygen towards new combinations which causes the explosion when oxidable elements are contained in the *same* compound, as the above peculiarity of nitrogen. Why does not nitric acid, when put upon copper, explode to form nitrogen, copper oxide and copper nitrate? The reason that nitro-products are so largely used for explosives is that they are practically manageable, that they are in other words, not the most explosive bodies. If it were possible to replace in nitroglycerine the three nitro groups by three  $\text{ClO}_2$  groups, we should have a more explosive compound. A mixture of potassium chlorate and permanganate can only be pulverized together with the utmost care, as the dry salts may blow up during this treatment. There is no nitrogenized explosive substance known which does not contain oxygen as well as nitrogen.

There are many chemical compounds containing nitrogen in a semi-molecular state, the so called diazo compounds which contain the chromogene group  $\text{N}_2$ , some of which are beautiful and toler-



ably fast dyes and not explosive, while it is easily understood that if such diazo compounds do decompose under the influence of chemical reaction, the nitrogen is set free as such in the molecular state, simply because this molecule of nitrogen exists two-thirds preformed in the substance. Also here we see a marked difference between nitrogen and oxygen. Oxygen in a semi-molecular state, so to speak, often shows a tendency to reform its molecule under explosion. Peroxide of hydrogen and the chlorine or iodine compounds of oxygen illustrate this fact.

It must not be forgotten that the oxygen molecule and the sulphur molecule, its analogue in this sense, may be considered as containing dipolar atoms which allow of free rotation around an axis formed by one of their valencies. *This* rotation does not exist in the trivalent nitrogen. The explanation does not seem to be remote, if we admit that this rotation, when suddenly *stopped* by the beginning of combination of oxygen with other elements, causes the production of heat and light. As long as this rotation is partly existing, however, as in the peroxides, the tendency to return to the molecular state is noticeable, considering that oxidation takes place at the same time if the opportunity is offered.

We may note here the fact that phosphorus, antimony and arsenic, represent elementary conditions of molecules similar to that of nitrogen. A difference in the behavior of chlorine compounds of these, when compared with nitrogen chloride, strongly supports our surmise that the atomic weight is one factor which influences the intensity of chemical attraction between atoms. The greater atomic weights of arsenic, phosphorous or antimony as compared with nitrogen prevent the influence of the heavy chlorine atom upon the curbing of the directions of their valencies as we supposed this to take place in nitrogen chloride.

It does not help our purpose here to consider the peculiarity of tri- and pent- atomicity of these elements. It is sufficient to say, that under certain conditions a body may be prevented from offering all its points of attack to a certain force. If we take a horseshoe magnet and only allow one of its poles to attract a piece of iron while the other remains free, we should not be allowed to speak of a unipolar magnet. We may consequently

settle this question here by assuming the higher number of valencies to be always shown when compounds exist at lower temperatures. If we surround phosphorus pentachloride with a heated mantle we attain a dissociation into chlorine and trichloride, similar to heated ammonium chloride which furnishes HCl and  $\text{NH}_3$  gas.

In many of the cases so far mentioned we recognized reactions, which in a former chemical period were spoken and thought of as taking place between the atoms as between animate beings, by predisposition rather to combine with this than with that element. The mere word affinity, changeable as the sense was in which it was applied at different periods, indicates this animation. The tendency of modern chemistry is to attempt to reduce these reactions to general principles of physics starting from chemical phenomena and remaining upon the chemical standpoint.

We must finally consider another case, which illustrates our endeavor. It is the one exemplified by chlorine, when acting upon bromides or iodides, when either bromine or iodine are liberated. We find here cases suggesting reversed conditions as we considered them in chloride of nitrogen and ammonia when compared. The chlorine atomically lighter than bromine is not able to influence the rotation of its unipolar ally hydrogen (as in hydrochloric acid) or of alkali metal in salts *as much* as the heavier bromine or the still heavier iodine. The compounds of iodine with metals show a remarkable tendency towards decomposition with formation of an iodine molecule, although the iodine compounds are still stable when compared to nitrogen chloride.

The *relative* intensity of the chemical force that acts between atoms to form molecules of elements or of chemical compounds must not be lost sight of in all our chemical views.

We have shown the strong points in favor of a more physical consideration of chemical phenomena from a chemical standpoint and it seems as if most chemical reactions might be satisfactorily explained in this way, even to-day.

NEWPORT, R. I., Aug. 7th, 1890.

## NOTE UPON BÜTSCHLI'S EXPERIMENTAL IMITATION OF PROTOPLASM.

BY C. A. SIEGFRIED, Surgeon U. S. Navy.

During the past few years Prof. Bütschli, of Heidelberg, has made many attempts, and now succeeds in producing under the microscope seemingly amœboid movements. He has communicated to Prof. Ray Lancaster, of England, a full account of his methods by which he attempts to imitate protoplasm. A medium sized watch glass or flat dish must be filled with a thin layer of common olive oil and be placed on a water bath or small cupboard at a temperature of about 50° C. The great point is to select the right moment at which the oil attains the proper degree of thickness and viscosity ; this moment can, however, only be found by systematic trials. After three or four days a trial may be made. Should the drop not have become finely vesiculate and exhibit little or no streaming, the heating process must be continued and a trial made on the succeeding day. If the oil becomes too thick it will form frothy drops, and in such cases a small quantity of ordinary olive oil must be mixed with it.

The vesiculate drops are thus prepared : In a small agate mortar a small quantity of dry carbonate of potash is ground to a fine powder. This is breathed on till the salt becomes slightly moist, and then a drop of oil must be added ; the two constituents should be mixed until they form a thickish paste. A few drops of this paste, about the size of a pin's head or smaller, are placed on a cover glass, the corners of which are supported by pegs of soft paraffin. Then a drop of water is placed on a slide and the cover glass is put over it in such a manner that the drops of paste

*Quarterly Journal Microscopical Science*, xxxi, 1890, pp. 99 and 103.  
*Journal Royal Microscopical Society*, 1889, p. 731, 1890, p. 403.

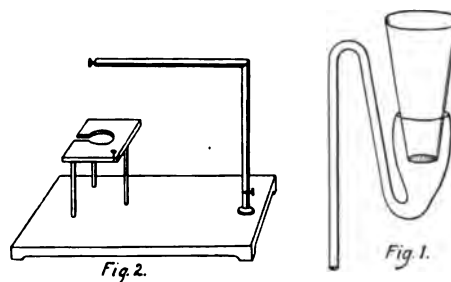
are immersed in the water, but are not much compressed. The preparation is then placed in a damp chamber, and remains there about twenty-four hours, when the drops have a milk white and opaque appearance. The preparation is then well washed out with water, which is supplied at one edge by a capillary tube and drawn out by blotting paper at another.

If the drops have turned out well they will begin almost at once to move about rapidly and change their shape continuously. The water under the cover glass must now be displaced by glycerine diluted with an equal bulk of water, when a vigorous streaming movement will be exhibited. The amoeboid movements are generally more distinct if the drops are somewhat compressed. If the drops do not stream they can be generally made to do so by slightly tapping the cover glass, by applying gentle pressure, or sometimes by breaking up the drops. It is especially interesting to see how fast and beautifully the drops creep to and fro in the water or half diluted glycerine, even when they are not compressed. The streaming movement on the other hand is better seen if the drops are somewhat compressed; this may be done by inserting under the cover glass a piece of broken cover glass of medium thickness, and then removing the paraffin pegs. This streaming movement is best demonstrated twenty-four hours after the addition of the glycerine, as the drops will then be thoroughly cleared and transparent. The movement and streaming are much more marked and distinct if the drops are examined on a stage warmed to 50° C. Prof. Bütschli advises repeated trials if the first experiments prove unsuccessful. Saponification, and vibratory movements inseparable from all inhabited spots, do not offer satisfactory solutions, and I take the liberty of asking the members of the Society for some little discussion regarding the probable causes concerned.

## THE USE OF THE GOOCH CRUCIBLE AS A SILVER VOLTAMETER.

BY DR. MORRIS LOEB.

For the exact measurement of electric currents, no method is more convenient and more free from objections than the determination of the amount of silver deposited from a neutral solution of a silver salt. The sole source of error, especially where weak currents are concerned, arises from the imperfect adhesion of the silver upon the cathode. The latter is generally a platinum crucible, and the silver, except for densities of current not always attainable, is deposited in minute scales and needles, instead of forming a coherent coating. In the subsequent washing and decantations, these particles are readily detached and carried away, and a loss is occasioned which becomes very appreciable when the total deposit does not exceed a few centigrams. A Gooch crucible, with asbestos felting over the holes, would be a far better form of cathode, if it would only hold the solution during electrolysis without leaking. I have attained this very satisfactorily, by replacing the ordinary platinum cap with a glass siphon of the shape indicated in Fig. 1.



The crucible is made on a rather taller and narrower pattern than is usual, and it fits quite snugly into the upper portion of the cup

of the siphon. The two are united by a bit of rubber drawn over the junction; the rubber should be freed from sulphur, although there is no real danger of contact with the silver solution.

The apparatus is filled with the silver nitrate solution, so that the top of the siphon is not quite reached and is set upon the stand, Fig. 2. After the completion of the electrolysis, adding a little liquid causes the siphon to act and to drain off every drop of nitrate solution, without in any way disturbing the deposit; the lixiviation with hot water is equally expeditious, and the crucible can then be detached from the siphon, dried and weighed.

The stand for this voltameter is seen in fig. 2. The crucible is hung in a brass block, the conical hole in which fits exactly around its upper third; to this block the negative wire of the circuit is to be attached.

The positive wire is connected with long horizontal cone, which is isolated from the cast-iron base, and from which the silver cone that forms the anode is suspended within the crucible by a silver wire.

## ON A NEW PROCESS FOR THE EXTRACTION OF INDIGOTIN FROM COMMERCIAL INDIGO.

BY THOS. M. MORGAN.

A few years ago I had occasion to use indigotin as pure as possible and in considerable quantities, for industrial purposes, and endeavored to obtain it from commercial indigo by some of the well known methods. Eventually I adopted the following process, which is easy of execution and gives a satisfactory yield.

Commercial indigo, finely ground and intimately mixed with about an equal weight of zinc dust is spread in layers, about an inch deep, on thin boards, and introduced into a steam chest so constructed that it can be closed air tight, and provided with a steam pipe for the introduction of steam and one for its exit; also with an aperture for the introduction of a solution of sulphurous acid. The indigo mixture is also screened, to prevent condensed steam dropping upon it. When these arrangements are complete the air is driven out by a rapid current of steam; then the steam valve is nearly closed, a little steam being allowed to pass through the apparatus, so as to prevent the entrance of air. Next the solution of sulphurous acid is introduced, a little at a time, so as to saturate the steam in the chest with sulphur dioxide, and it is maintained in this condition while the reduction of the indigo is going on.

The reaction between the zinc, sulphur dioxide and indigotin goes on rapidly, and in about one or two hours the indigotin should be completely reduced. It then presents a dirty yellow or greenish yellow color, and when it dries, which it quickly does on taking from the steam chest, is not liable to rapid oxidation, but may be kept for several days without much change. From the mixture the indigo white may be recovered in an extraction apparatus by means of wood spirit, or by digestion in flasks filled to the neck with the same solvent. On exposure of the solution in shallow vessels to the air the indigotin is precipitated pure and crystalline. The yield is large, and probably a theoretical one when all necessary precautions are employed.

## FLUORIDES AS AGENTS FOR SOFTENING HARD WATERS.

CHARLES A. DOREMUS, M. D., PH. D.

A study of the various chemicals that might prove serviceable for softening water was begun as the result of my attention having been directed to the very serious difficulties that are met with in the practical use of lime, soda ash and caustic soda. Early in the work the fluorides, such as sodium fluoride, seemed to offer a fruitful field of investigation and subsequent events proved that not only sodium fluoride, but other fluorine compounds possess admirable qualities for these uses.

Laboratory experiments were first made with sodium fluoride alone and also in conjunction with other chemicals. These were followed by experiments on a large scale, the results of which were very satisfactory. The precipitation of magnesium is especially thorough and noteworthy. These experiments have since been extended and have passed also into a regular employment of the chemical.

The fluorides do not appear to have as yet had any extended commercial use, nor to have been applied heretofore for treating water. Failure to find any mention of such fact in chemical literature has been supplemented by a similar failure on the part of Patent Office officials here and abroad to discover any to cite in interference.

One of the chief difficulties met with in the pursuit of the work was my inability to obtain in open market any fluoride in quantity, or at any but an exorbitant price. This has been so far overcome that sodium fluoride has been manufactured for me in large quantities at a figure which to the consumer will not prove prohibitive.

COLLEGE OF THE CITY OF NEW YORK, August 7, 1890.



## MINUTES OF SEPTEMBER MEETING.

\*REGULAR MEETING, Sept. 19, 1890.

Vice-President Breneman in the chair.

The Corresponding Secretary, Dr. Hale, read the minutes of the Newport meeting which were accepted as read.

The following gentlemen were elected to membership :

Dr. Lewis H. Laudy, School of Mines, N. Y.

Chas. A. Pitkin, A.M.Ph.D., Coll. Phys. and Surg., Boston, Mass.

Major W. R. Livermore, U. S. A., Newport, R. I.

Mr. G. W. Patterson, Newport, R. I.

The following names were proposed for membership :

Stephen H. Emmens, Emmensite Explosive Co., Emmens, Pa.

F. E. Thompson, Headmaster Rogers High School, Newport, R. I.

Dr. Geo. Archbold, Chemist U. S. N., Washington, D. C.

Prof. G. C. Caldwell, Professor of Agricultural Chemistry, Cornell University, Ithaca, N. Y.

Chas. E. Colby, Ph.D., Professor of Organic Chemistry, School of Mines, N. Y.

Prof. W. H. Seaman, Professor of Analytical Chemistry, Missouri School of Mines, Rolla, Mo.

Dr. Chas. E. Pellew, School of Mines, N. Y.

Hugh Hamilton, M.D., Harrisburg, Pa.

Edward Gudeman, Honorary Assistant in Chemistry, School of Mines, N. Y.

Dr. Alfred Springer, Pres. Springer Torsion Balance Co., 46-50 E. 2d street, Cincinnati, O.

Dr. H. J. Wheeler, Chemist Agricultural Experiment Station, Kingston, R. I.

Dr. Edward S. Wood, Professor of Chemistry, Harvard Medical School, Cambridge, Mass.

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\* Adjourned from Sept. 5, 1890.

Dr. S. A. Lattimore, Professor of Chemistry, University of Rochester, Rochester, N. C.

Prof. Chas. E. Brewer, Professor of Chemistry, Wake Forest University, Wake Forest, N. C.

Prof. R. W. Jones, Professor of Chemistry, University of Mississippi, Oxford, Miss.

Prof. Peter T. Austen, Professor of Chemistry, Rutgers College, New Brunswick, N. J.

Mr. Harry Snyder, Instructor in Chemistry, Cornell University, Ithaca, N. Y.

Dr. Chas. G. Curtman, 3718 N. 9th street, St. Louis, Mo.

B. B. Goldsmith, Ph.B., Chemist American Lead Pencil Co., 19 E. 74th street.

F. A. Owen, S.B., Chemist Burlington Woolen Co., Burlington, Vt.

The following name was proposed for associate membership :  
S. V. V. Huntington, Manager Edw. Smith & Co., 158 William street, N. Y.

As a result of a discussion upon the relation of general meetings to regular meetings a motion was made to refer the question to the Board of Directors for consideration and a subsequent report to the Society. Carried. The meeting was then adjourned.

CHAS. F. MCKENNA,

Recording Secretary.

### **OBITUARY.**

SILAS H. DOUGLAS died in Ann Arbor, Mich., August 26, 1890, at the age of seventy-four years. He has been professor of chemistry in the University of Michigan from 1846 to 1877. The chemical laboratory of this institution, erected in 1856 and repeatedly extended, was the product of his labors, continued with energy through the active portion of his life. For a number of years his health has been infirm, and he has remained in the retirement of his devoted family.

# ON BLAST FURNACE SLAGS AND THE FUSIBILITY OF SILICATES.

BY AUGUSTÉ J. ROSSI.

(Concluded.)

An examination of a few specimens of natural silicates occurring as ordinary minerals and of which the composition is very often reproduced artificially in blast furnaces, will corroborate the preceding statement that, in a slag, in a multiple silicate, the silicates of the bases RO and  $R_2O_3$  are of the same type. The following examples are taken from a table of silicates by Prof. Eggleston, of Columbia College, in which the old formula for silica,  $SiO_3$ , is used :

*Orthoclase*. \*—O Ratio,  $\frac{R_2O}{1} : \frac{R_2O_3}{3} : \frac{SiO_3}{12}$  or

RO,  $SiO_3 + Al_2O_3$ ,  $3SiO_3$  (Trisilicate of Percy), or, written with  $SiO_2$ ,  $2RO \ 3SiO_2 + 2R_2O_3 \ 9SiO_2$ . Total—O of  $SiO_2$  : O of bases :  $24 : 8 = 12 : 4 = 3 : 1$ , a *sesqui-acid silicate* ; the O ratio for each silicate is 3 : 1 in both formulæ, as for the mineral itself. It is the tri-silicate of the present time derived from  $H_4Si_3O_8 = 2(H_2O)3SiO_2$ . O ratio  $6 : 2 = 3 : 1$ .

*Sodalite*. \*—1 : 3 : 4.  $3NaO$ ,  $SiO_3 + 3(Al_2O_3, SiO_3)$ . (Tribasic or monosilicate of Percy). Formula, with  $SiO_2$ ,  $2NaO \ SiO_2 + 2R_2O_3 \ 3SiO_2$ . *Bibasic silicate*. O ratio 1 : 1 for each silicate, for the compound  $12 : 12 = 1 : 1$  ; derived from  $H_4SiO_4 = 2(H_2O)SiO_2$ , a monosilicate or orthosilicate with O ratio ;  $2 : 2 = 1 : 1$ .

*Anorthite*.—1 : 3 : 4.  $3CaO$ ,  $SiO_3 + 3(Al_2O_3, SiO_3)$  the same as sodalite, O of acid, : O of bases =  $3 : 3 = 1 : 1$  ; or with  $SiO_2$ ,  $2CaO \ SiO_2 + 2Al_2O_3 \ 3SiO_2$  a *bibasic silicate*. O of acid : O

\* Found in the United States.

of base=2 : 2=6 : 6=1 : 1 for each silicate and for the compound.

*Epidote*.—1 : 2 : 3 or  $3R_2O \cdot SiO_3 + (R_2O_3 \cdot SiO_3)$ ; O ratio 1 : 1 the same as sodalite, a *bibasic silicate*  $2RO, SiO_2 + 2R_2O_3, 3SiO_2$ ; O ratio of compound 1 : 1, of each silicate 1 : 1.

*Garnet*.—1 : 1 : 2,  $3RO \cdot SiO_3 + R_2O_3 \cdot SiO_3$ . Oxygen ratio 1 : 1 for each silicate and for the compound; now a *bibasic silicate*,  $2RO \cdot SiO_2 + 2R_2O_3 \cdot 3SiO_2$  O ratio 1 : 1. Pyrope  $3(CaO, MgO) \cdot SiO_3 + (Al_2O_3 \cdot Fe_2O_3) \cdot SiO_3$ .

*Prehnitoid*.—1 : 2 : 6,  $3RO \cdot 2SiO_3 + 2(Al_2O_3 \cdot 2SiO_3)$  (sesquibasic or bisilicate of Percy), O ratio 6 : 3 for each silicate=2 : 1; for the compound 18 : 9=2 : 1; or with  $SiO_2 : RO, SiO_2 + R_2O_3 \cdot 3SiO_2$ , a *neutral silicate*; O ratio of each silicate 2 : 1; of the compound 2 : 1. It is monosilicate of modern nomenclature derived from  $H_2SiO_4 = H_2O \cdot SiO_2$ ; O ratio 2 : 1.

*Petalite*.—1 : 4 : 20,  $3RO \cdot 4SiO_3 + (Al_2O_3 \cdot 4SiO_3)_4$  O ratio for the compound and for each silicate 60 : 15=12 : 3=12 : 3=4 : 1, an *acid silicate*, or with  $SiO_2 : RO \cdot 2SiO_2 + R_2O_3 \cdot 6SiO_2$ ; O ratio for the compound and for each silicate 16 : 4=12 : 3=4 : 1; the disilicate of modern nomenclature derived from  $H_2Si_2O_6 = H_2O \cdot 2SiO_2$ ; O ratio 4 : 1.

*Chloritoid*.—1 : 2 : 2 : 1 Aq.,  $3RO \cdot SiO_3 \cdot \frac{2}{3} + 2(R_2O_3 \cdot SiO_3 \cdot \frac{2}{3}) + 3HO$ ; multiplying by 3 we have  $9RO \cdot 2SiO_3 + 2(3R_2O_3 \cdot 2SiO_3) + 9HO$ . O ratio compound = 18 : 27=2 : 3. For each silicate 6 : 9=6 : 9=2 : 3; or with  $SiO_2 : 3RO \cdot SiO_2 + R_2O_3 \cdot SiO_2$ , a *tribasic silicate*; O ratio for the compound and each silicate=2 : 3 derived from  $H_6SiO_6 = 3(H_2O) \cdot SiO_2$ ; a parasilicic monosilicate; O ratio 2 : 3.

(a.) Assume that we have a slag having a composition corresponding to  $RO \cdot 2SiO_2 + R_2O_3 \cdot 6SiO_2$  an acid silicate of the same type in  $RO + R_2O_3$ ; O ratio for each 4 : 1; for compound 4 : 1; it corresponds to the following proportions:

1°. $SiO_2 = 75.120$	} We find, transforming all the bases into lime,	
$(CaO)RO = 8.763$		$SiO_2 68.19$
$Al_2O_3 = 16.117$		$CaO 31.81$
100.000		100.00 an acid silicate as

we can see from the Table V., O ratio=4 : 1. The transformation

into lime has *at once* furnished us the type of the silicate without using any formula or symbol.

2°. Let us calculate the formula of this slag by the determination of the oxygen of the constituents: We have

Oxygen.

$$\begin{array}{l} \text{SiO}_2 = 75.120 \text{-----} 40.08 \\ \text{CaO} = 8.763 \text{-----} 2.507 \\ \text{Al}_2\text{O}_3 = 16.117 \text{--} 7.521 \end{array} \left\{ \begin{array}{l} \text{O of acid} = 40.08 = \text{O} \\ \text{of bases } 10.02 \times 4; \\ \text{the type is acid. Pro-} \\ \text{portioning the O of} \\ \text{silica to that of the} \end{array} \right. \text{-----} 10.028$$

bases we find:

$$\frac{2 \times 507 \times 40.06}{10.028} = 10.028 \text{ O of silica in RO, or } 5.014 \text{ SiO}_2 \text{ with}$$

RO; we have 2.507 O in RO, the formula is 2.507 RO, 5.014 SiO<sub>2</sub>.

O of silica in R<sub>2</sub>O<sub>3</sub> = 40.08 — 10.028 = 30.05, or 15.025 SiO<sub>2</sub>, combined with R<sub>2</sub>O<sub>3</sub>.

O of R<sub>2</sub>O<sub>3</sub> = 7.521 = 2.507 R<sub>2</sub>O<sub>3</sub>. Formula: 2.507 R<sub>2</sub>O<sub>3</sub>, 15.025 SiO<sub>2</sub> or

2.507 (RO 2SiO<sub>2</sub>) + 2.507 (R<sub>2</sub>O<sub>3</sub> 6SiO<sub>2</sub>) a perfect acid silicate of bases in RO and in R<sub>2</sub>O<sub>3</sub>. O ratio 4 : 1, the same result as obtained by transformation into lime.

3°. Let us calculate the empirical formula from the equivalents:

$\begin{array}{l} \text{SiO}_2 = 75.120 = 2.50 \text{ Eq., or } 8. \\ \text{CaO} = 8.763 = 0.313 \text{ Eq., or } 1. \\ \text{Al}_2\text{O}_3 = 16.117 = 0.313 \text{ Eq., or } 1. \end{array} \left\{ \begin{array}{l} \text{Hence, the empirical formula} \\ \text{is (RO R}_2\text{O}_3\text{)8SiO}_2, \text{ and} \\ \text{O of silica : O of bases : :} \end{array} \right.$   
16 : 4 = 4 : 1 as before. The type is an acid silicate as found at once by transformation into lime. But as may be seen, the empirical formula does not furnish any indication as to the grouping of the elements. If we are to be guided by the oxygen ratio of the compound, then the only rational formula is: RO 2SiO<sub>2</sub> + R<sub>2</sub>O<sub>3</sub> 6SiO<sub>2</sub> and fatty silicate in RO and R<sub>2</sub>O<sub>3</sub> are of the same type.

(b.) Let us assume now that we have a substance of the following composition:

R<sub>2</sub>O<sub>3</sub> 3SiO<sub>2</sub> (Neutral) + 2RO SiO<sub>2</sub> (Bibasic). Such a compound may certainly exist, but, if run in a blast furnace, since R<sub>2</sub>O<sub>3</sub> 3SiO<sub>2</sub> as well as 2RO SiO<sub>2</sub> are both refractory or very little fusible, (see fusibility of silicates), let RO be MgO or CaO,

and let  $R_2O_3$  be  $Al_2O_3$ ; there must certainly be such a combination of the two types, such an exchange of the bases as will no longer correspond to a saturation of  $1R_2O_3$  for  $3SiO_2$  and of  $2RO$  for  $1SiO_2$ , but will furnish a different one corresponding to a unique type or the multiple silicate, and one which must be the same for the bases in  $R_2O_3$  and those in  $RO$ .

This formula leads to the following composition :

$SiO_2 = 52.747$  } In the table of fusibility, we see that 58  
 $CaO = 24.615$  } silica, 16 alumina and 26 lime give a *very*  
 $Al_2O_3 = 22.637$  } *fusible* silicate. A silicate of the annexed  
 composition would therefore fuse readily in the blast furnace, but  
 if we proportion the silica according to the above formula  $R_2O_3$ ,  
 $3SiO_2 + 2RO$ ,  $SiO_2$ , we come to

$21.10 SiO_2$  } or about 46CaO to 56SiO<sub>2</sub>, the "simple sili-  
 $24.61 CaO$  } cate" begins to be barely "fusible," and at  $SiO_2$  31.67,  $Al_2O_3$   
 22.63, or about 58  $SiO_2$  to 42  $Al_2O_3$ , the simple silicate is absolutely  
 refractory, it must certainly be then by different saturation of  
 silica to form a unique type that these proportions of silica, lime  
 and alumina furnish a fusible compound.

Transforming *all* into lime, we obtain the following percent-  
 age :
 
$$\left. \begin{array}{l} SiO_2 = 46.164. \\ CaO = 53.836. \end{array} \right\}$$

(O of acid = 1.6 O of bases) which, falling between a sesquibasic and a neutral silicate (Table V.) represents a sufficiently fusible slag. This transformation gives us at once an approximation of basicity of the slag and the type of the silicate.

3°. If we calculate the formula from the oxygen of the compounds, we find :

$O \text{ of Silica} \dots\dots\dots 28.131$  }  $O \text{ of acid} : O \text{ of bases} ::$   
 $O \text{ of RO} \dots\dots\dots 7.033$  }  $28.131 : 15.95 = 1.6 : 1$   
 $O \text{ of } R_2O_3 \dots\dots\dots 10.562$  }  $15.95$  } as before. If we propor-  
 tion the O of silica to that of the bases in  $RO$  and  $R_2O_3$ , we find  
 for the formula :

$5.61 SiO_2$   $7.033 RO$  +  $8.45 SiO_2$   $3.52 R_2O_3$ , or  $3.52 (R_2O_3$   
 $2.4 SiO_2)$ , O ratio  $4.8 : 3 = 1.6 : 1$  +  $5.61 (1\frac{1}{2} RO, SiO_2)$   
 O ratio  $2 : 1\frac{1}{2} = \frac{4}{3} : \frac{3}{2} = 8 : 5 = 1.6 : 1$  the silicates in  $RO$   
 $2R_2O_3$  are of the same type and of the same type as the com-  
 pound itself.

$R_2O_3$ ,  $2.4 SiO_2$  is less neutral or *more basic* than  $R_2O_3$ ,  $3SiO_2$ , a neutral silicate, but *less basic* than  $R_2O_3$ ,  $2SiO_2$ , a sesquibasic silicate; the same for the silicates in RO, the slag as given by the formula falls between a neutral and a sesquibasic slag; just what the transformation into lime had given us.

4°. If we calculate the equivalents, we have :

$$\begin{array}{rcl} SiO_2 = 52.747 = 1.758 \text{ Eq. of } SiO_2 & & 4 \\ CaO = 24.615 = 0.879 \text{ Eq. of } CaO & \text{or} & 2 \\ R_2O_3 = 22.637 = 0.439 \text{ Eq. } Al_2O_3 & & 1 \end{array}$$

The empirical formula is  $(2RO, R_2O_3)4SiO_2$ . O ratio is  $8 : 5 = 1.6 : 1$ , just what has been furnished to us by the transformation in lime. But the empirical formula does not afford any means of grouping the elements.

Two types satisfy the condition  $(2RO, R_2O_3)4SiO_2$ ; they are :

$2RO, SiO_2$  (Bibasic) and  $R_2O_3, 3SiO_2$  (Neutral), or  $2RO, 3SiO_2$  (Sesquiacid) +  $R_2O_3, SiO_2$  (Tribasic).

The first corresponds to the formula which has given us the preceding composition, but the second does not, and we have no way to choose *a priori*. If we take as a guide the O ratio, which has been found to be 1.6 to 1 *for the compound*, we reach the preceding formulæ,  $R_2O_3, 2.4SiO_2 + 1.25RO, SiO_2$  or  $5R_2O_3, 12SiO_2 + 5RO, 4SiO_2$ . O ratio =  $24 : 15 = 8 : 5 = 1.6 : 1$  for  $R_2O_3$ , and the same for the silicate in RO,  $8 : 5 = 1.6 : 1$ .

(c.) Suppose now that we have a slag of the same type in RO and  $R_2O_3$  (Neutral), we are at perfect liberty to admit a composition as follows :

$2(R_2O_3, 3SiO_2) + 4(RO, SiO_2)$ , as indeed the O ratio :  $8 + 12 = 20$  oxygen of acid :  $4 + 6 = 10$  oxygen of bases : :  $2 : 1$  (type neutral), is not changed. It corresponds to :

$$\begin{array}{rcl} 1^\circ. & SiO_2 & = 58.25 \\ & CaO & = 21.74 \\ & Al_2O_3 & = 20.00 \end{array}$$

99.99

Calculating the formula we have O of  $SiO_2 = 31.06$ ; O of RO = 6.21;  $OR_2O_3 = 9.33$ ; 6.21 (RO,  $SiO_2$ ) + 3.11 ( $R_2O_3, 3SiO_2$ ) a perfectly neutral silicate in RO and  $R_2O_3$ . O of silica for each : O of base : :  $2 : 1 : : 6 : 3$ .



And 6.21 of neutral silicate in RO : 3.11, of neutral silicate in  $R_2O_3$  : : 4, of neutral silicate in the compound : 2, of neutral silicate in the compound = 2 : 1.

The relative proportion of each is maintained.

2°. Transforming *all into lime* we would have found *at once*, without symbols or formulæ :

$$\begin{array}{rcl}
 SiO_2 & = 58.25 & \dots\dots\dots 58.25 \\
 CaO & = & \dots\dots\dots 21.74 \text{ CaO} \\
 Al_2O_3 & = 20 \times 1.631 = & 32.625 \text{ CaO} \\
 & & \hline
 & 54.365 & \dots\dots\dots 54.36 \\
 & & \hline
 & & 112.61
 \end{array}$$

Or reducing to percentage :

$$\begin{array}{rcl}
 SiO_2 & = & 51.72 \\
 CaO & = & 48.28
 \end{array}$$

a typical neutral silicate, Table V.

3°. If we calculate the equivalents, we have :

$$\begin{array}{rcl}
 SiO_2 & = & 1.941 \quad 5 \\
 CaO & = & 0.776 \quad \text{or} \quad 2 \\
 R_2O_3 & = & 0.388 \quad 1
 \end{array}$$

And the empirical formula is  $(R_2O_3 \ 2RO)5SiO_2$ , O of silica 10 : O of bases 5 : : 2 : 1 ; the type is neutral.

But if we do not take this as a guide, we can group the bases and the silica in the following manner :

$$\begin{array}{l}
 1^\circ. \quad \underbrace{2(RO \ 2SiO_2)}_{\text{Acid silicate}} + \underbrace{R_2O_3 \ SiO_2}_{\text{Tribasic}}; \text{ or} \\
 2^\circ. \quad \underbrace{2RO \ 3SiO_2}_{\text{Sesquiacid}} + \underbrace{R_2O_3 \ 2SiO_2}_{\text{Sesquibasic}}; \text{ or}
 \end{array}$$

4°.  $2RO \ SiO_2$  (Bibasic) +  $R_2O_3$ ,  $4SiO_2$  (?), and we have no way to choose which is the rational formula. If we adopt the O ratio furnished by the compound, then the *only rational formula* is:  $2(RO \ SiO_2) + R_2O_3 \ 3SiO_2$ , and the silicates in  $R_2O_3$  and in RO are again of the same type; furthermore this gives 2 of silicates in RO for 1 of silicate in  $R_2O_3$ , the same proportions

as in the original compound. The transformation into lime has furnished us at once the character of the slag.

We will complete these illustrations by a few examples of slags actually run in blast furnaces, and of which the composition is given in standard books on metallurgy (Percy and others).

Percy gives as the composition of a slag, run in a coke furnace, with hot blast, iron gray :

SiO<sub>2</sub> 38.00.....O 20.26. O of acid=very nearly O of bases,  
type *bibasic*.

Al <sub>2</sub> O <sub>3</sub>	14.00	.....	6.53	} 20.09	O of SiO <sub>2</sub> in R <sub>2</sub> O <sub>3</sub> =6.53 or
CaO	33.50	.....	9.57		3.26 SiO <sub>2</sub> (exactly : 3.29)
MgO	6.50	.....	2.60		O of SiO <sub>2</sub> in RO=13.56 or
MnO	2.50	.....	0.55		6.78 SiO <sub>2</sub> (exactly : 6.84).
FeO	2.00	.....	0.44		
K <sub>2</sub> O	2.00	.....	0.40		

The formula is 2RO, SiO<sub>2</sub> (bibasic) + 2R<sub>2</sub>O<sub>3</sub>,  
3SiO<sub>2</sub> (bibasic) O of acid : O of bases : 1 : 1.

Established from the O ratio or transformed from the formula in SiO<sub>2</sub>, the formula in SiO<sub>3</sub> is (R<sub>2</sub>O<sub>3</sub> SiO<sub>3</sub>) 2.18+4.52 (3RO SiO<sub>3</sub>): O of acid for each silicate: O of base : : 1 : 1; total oxygen of bases=(3×4.52+2.18×3)=20.10; O of acid=(2.18×3+3×4.52)=20.10=O of bases.

Percy gives as an approximate formula: “(R<sub>2</sub>O<sub>3</sub> SiO<sub>3</sub>+3RO SiO<sub>3</sub>)” which is the type formerly called tribasic or monosilicate, now called *bibasic* in SiO<sub>2</sub>: as 3SiO<sub>2</sub>=2SiO<sub>3</sub>.

This is the mineral called “Mellilite”: 2(3CaO, MgO, NaO) SiO<sub>3</sub>+(Al<sub>2</sub>O<sub>3</sub>Fe<sub>2</sub>O<sub>3</sub>)SiO<sub>3</sub>. If we had transformed the slag at once into lime we should have found without any formula or symbol :

SiO <sub>2</sub> =38.00	.....	38.00	SiO <sub>2</sub>
Al <sub>2</sub> O <sub>3</sub> =14.00×1.631		22.83	CaO
CaO=33.50	.....	33.50	“
MgO=6.50×1.40=		9.10	
MnO=2.50×0.78=		1.95	
FeO=2.00×0.78=		1.56	
K <sub>2</sub> O=2.00×0.59=		.24	

---

69.18

Or :	SiO <sub>2</sub>	38.00, or in %, SiO <sub>2</sub> =35.45-----	34.88
	CaO	69.18	CaO=64.55----- 65.12
		<hr/>	<hr/>
		107.10	100.00      100.00
			type bibasic.
			(Table V.)

Percy gives the composition of a slag from blast furnaces of Olsberg on the Rhine :

## OXYGEN.

SiO <sub>2</sub>	53.76-----	28.67	O of acid 28.67: O of bases 15.07
			=1.90 : 1, or nearly 2 : 1 <i>type</i>
Al <sub>2</sub> O <sub>3</sub>	4.76-----	2.22	<i>neutral</i>
CaO	29.48-----	8.42	O of Silica in R <sub>2</sub> O <sub>3</sub> =4.35=1.45 SiO <sub>2</sub> O of Silica in RO=24.32=8.11 SiO <sub>2</sub>
MnO	1.30-----	0.30	
FeO	1.48-----	0.33	
MgO	9.50-----	3.80	
			12.85
			15.07

Formula : 0.74 R<sub>2</sub>O<sub>3</sub>, 1.45 SiO<sub>2</sub>, or, 0.74 (R<sub>2</sub>O<sub>3</sub>, 2SiO<sub>2</sub>)  
12.85 RO, 8.11 SiO<sub>2</sub>, or, (3RO 1.90 SiO<sub>2</sub>) 4.28.

Percy says : Very nearly “(R<sub>2</sub>O<sub>3</sub> 2SiO<sub>2</sub>+3RO 2SiO<sub>2</sub>)” or, in SiO<sub>2</sub>, RO SiO<sub>2</sub>+R<sub>2</sub>O<sub>3</sub>3SiO<sub>2</sub>, a neutral silicate in RO and R<sub>2</sub>O<sub>3</sub>. It is the mineral called *Augite*, containing aluminium silicate, aluminiferous Augite or Pyroxene 3(CaO MgO) 2SiO<sub>2</sub>.

Transformed into lime we find at once :

SiO <sub>2</sub>	=53.76
Al <sub>2</sub> O <sub>3</sub>	=4.76×1.631 = 7.76 CaO
CaO	=-----=29.48
MnO	=1.30×.78=----- 1.01
FeO	=1.48×.78=----- 1.15
MgO	=9.50×1.40=-----13.30
	<hr/>
	52.70

Or, SiO <sub>2</sub>	53.76	reducing to	SiO <sub>2</sub> =50.50-----	SiO <sub>2</sub> = 51.71
CaO	52.70	percentage	CaO = 49.50-----	CaO = 48.28
	<hr/>		<hr/>	<hr/>
	106.46		100.00	100.00

Very nearly a neutral slag as found before.

O ratio : 2 : 1

We see, from the preceding examination, that in slags corresponding in composition to certain minerals, slags actually run in blast furnaces or in slags made up *a priori* from a given formula, as well as in natural minerals themselves, as quoted from table of such silicates, the individual silicates in RO and  $R_2O_3$ , have been found to be of the same type, which is the type of the compound itself characterized by a certain *ratio of the total oxygen of  $SiO_2$  to that of the bases*. Whatever may be the relation of the oxygen of the bases in RO, to the oxygen of the bases in  $R_2O_3$ , if it is rational to say that the amounts of silica combined with each class of oxide must bear a certain relation to the quantities of oxygen contained in each, we are then justified in dividing the oxygen of the silica proportionally to these numbers. By so doing we must find constantly as the quota of oxygen of the silica combined with the bases RO and  $R_2O_3$ , figures which will give for the silicates of RO and  $R_2O_3$  a ratio of O of acid to O of the base precisely the same as that of the compound itself, since in each case the calculation is established as follows: Total O of silica = m, O of RO = a, O of  $R_2O_3$  = b, and total O of bases = a + b. Ratio of the total O of  $SiO_2$  to total O of bases in the compound =  $\frac{M}{a+b}$ .

$$\text{O of silica combined with } R_2O_3 = \frac{M \times b}{a+b}$$

O of silica combined with

$$RO = M - \frac{Mb}{a+b} = \frac{Ma + Mb - Mb}{a+b} = \frac{Ma}{a+b}$$

$$\text{and } \frac{Ma}{a+b} \text{ O of silica as silicate of RO : a O of RO} = \frac{M}{a+b}$$

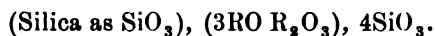
$$\frac{Mb}{a+b} \text{ O of silica as silicate of } R_2O_3 : b \text{ O of } R_2O_3 = \frac{M}{a+b}$$

the O ratio of the compound itself.

*The rational* formula of a silicate cannot be established otherwise than by taking as a guide the O ratio, the only clear and indisputable character furnished directly by the analysis. The use of the equivalents or atomic weights, as we have seen, gives an *empirical*

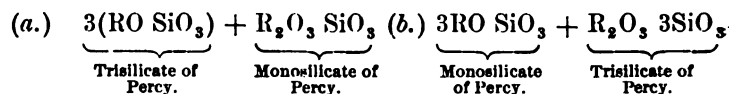
*formula* which allows of the grouping of the constituents in different manners; some of them not corresponding at all with the formula of the compound taken as basis of composition *a priori*.

For example: A slag run with white iron calculated in equivalents gave

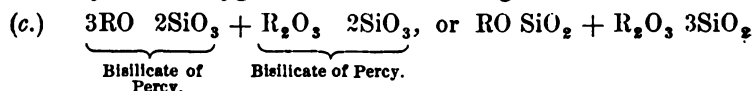


It can be grouped as follows:

O ratio 12 : 6 or 6 : 3 = 2 : 1 *Neutral*



and, lastly, if the oxygen ratio is taken as a guide



a neutral silicate in RO and  $\text{R}_2\text{O}_3$ .

In all cases, whether the *empirical* or the *rational* formula be adopted, we can obtain immediately, without the use of any symbol, by a simple multiplication and reduction to a percentage, all the elements necessary to judge of the "basicity" of a slag, of its approximation to certain types, and consequently of its fusibility as well as all the data for comparison with any other of different composition. All that is necessary is to transform all the bases into their equivalent in lime, as has been explained.

By such transformation we do not alter in any manner the type of the silicate, its oxygen ratio.

The characteristic feature of a silicate being afforded by the proportion of the oxygen of the acid to that of the base, if, in such a compound, a neutral silicate for instance,

$$\begin{aligned} \text{SiO}_2 &= 51.72 \\ \text{RO} = \text{CaO} &= 48.28 \\ \text{O ratio } &2 : 1 \end{aligned}$$

the quantity of  $\text{R}^1\text{O}$  (magnesia for example) which replaces a certain quantity of lime bears a direct proportion to their saturation for  $\text{SiO}_2$ , which, for this class of oxide  $\text{MO}$ , is as to that of their equivalent  $\text{R}^1\text{O}$  and RO, it is evident that the silicate *will pre-*

serve its type, the oxygen ratio of the silica remaining the same and being still double that of the base.

This can be established in an absolutely general manner as follows :

1°. Let

$$\begin{array}{l} \text{SiO}_2 = a \\ \text{CaO} = \text{RO} = b \end{array}$$

be a regular type of silicate of any kind for which we know that

$$\text{O of silica} = k, \text{ O of base. O of SiO}_2 = \frac{8}{15} a. \text{ O of CaO} = \frac{2}{7} b,$$

and we have, as characteristic of the compound,

$$\frac{8}{15} a = \frac{2b}{7} \times k.$$

Let us first replace any part  $b'$  of the weight  $b$  of lime by a weight  $b''$  of MgO, saturating the same quantity of silica as  $b'$  of lime, thus  $b''$  magnesia :  $b'$  lime : : 20 equiv. of MgO or 40 atomic weight of MgO : 28 eq. of lime or 56 atomic weight of lime

$$= 5 : 7 \quad \frac{b''}{b'} = \frac{5}{7}; \quad b'' = \frac{5}{7} b',$$

the composition of the silicate may be written then :

$$\begin{array}{l} \text{SiO}_2 = a \\ \text{CaO} = b - b' \\ \text{MgO} = b'' = \frac{5}{7} b' \end{array}$$

the O of the silica in the new compound

$$= \frac{8}{15} a = \frac{2b}{7} \times K$$

$$\text{as above. O of bases} = \frac{2}{7} (b - b') \text{ O of lime} + \underbrace{\frac{2}{5} \times \frac{5b'}{7}}_{\text{O of MgO}} \text{ O of MgO}$$

$$\text{O of bases} : = \frac{2b}{7} - \frac{2b'}{7} + \frac{2b'}{7} = \frac{2b}{7}$$

O of acid  $= \frac{2b}{7} \times k =$  O of bases  $\frac{2b}{7} \times k$  as before. The silicate *has maintained its type*, whatever it may have been originally, and whatever may have been the quantities a, b, k, b', b''.

2°. But if we replace the total weight b of lime by any weight b' of CaO and b'' of MgO, such that  $b' + b'' = b$ , the composition of the silicate becomes

$$\begin{aligned}\text{SiO}_2 &= a \\ \text{CaO} &= b' \\ \text{MgO} &= b'' = b - b'\end{aligned}$$

the O of silica is always

$$\frac{8}{15} a = k \frac{2b}{7}$$

$$\begin{aligned}\text{The oxygen of the bases} &= \frac{2}{7} b' + \frac{2}{5} (b - b') = \frac{2b'}{7} + \frac{2b}{5} - \frac{2b'}{5} = \\ &= \frac{10b' + 14b - 4b'}{35} = \frac{14b - 4b'}{35}\end{aligned}$$

Let b' be any part whatsoever of b  $= \frac{mb}{n}$  we have then :

$$\text{O of bases} = \frac{14b - 4b'}{35} = \frac{14b - 4 \times \frac{mb}{n}}{35} = \frac{14bn - 4mb}{35n} = \frac{2b}{7} \times \frac{7n - 2m}{5n}$$

and, O of acid :

$$\frac{2b}{7} \times k \text{ is no longer equal to } \text{O of bases } \frac{2b}{7} \times k; \text{ the type is changed,}$$

but, if  $\frac{7n - 2m}{5n} = 1$  we return to the original silicate, this will happen if  $n = m$ .

$m=1$  then  $\frac{7n - 2m}{5n} = \frac{7m - 2m}{5m} = 1$ ;  $b = b'$  and the composition becomes

$$\left. \begin{aligned}\text{SiO}_2 &= a \\ \text{CaO} &= b \\ \text{MgO} &= b - b' = b'' = 0\end{aligned} \right\} \text{O of acid } \frac{2b}{7} \times k = \text{O of bases } \frac{2b}{7} \times k \text{ as it should be.}$$





$$\left( \frac{2b}{7} - \frac{2b'}{7} \right) + \frac{24b'}{84} = \frac{2b}{7} - \frac{2b'}{7} + \frac{2b'}{7}$$

$$\text{O of acid} = \frac{8}{15}a = \frac{2b}{7} \times k$$

$$\text{Total O of bases} = \frac{2b}{7} - \frac{2b'}{7} + \frac{2b'}{7} = \frac{2b}{7} \text{ and}$$

O of acid = O of bases  $\frac{2b}{7} \times k$  as before, the type has not been changed.

Let us calculate the formula of the compound in this case.

$$\text{O of RO} = \frac{2b-2b'}{7}; \text{ O of R}_2\text{O}_3 = \frac{2b'}{7}$$

$$\text{Total O of acid} = \frac{8}{15}a = \frac{26}{7} \times k.$$

$$\text{Total O of bases} = \frac{26}{7} = \left\{ \begin{array}{l} \text{O, O of RO} = \frac{2b-2b'}{7} \\ + \text{O}_3, \text{ O of R}_2\text{O}_3 = \frac{2b'}{7} \end{array} \right.$$

$$\text{O of acid} \frac{2b}{7} \times k = \text{O of bases} \frac{2b}{7} \times k.$$

Proportioning the O of SiO<sub>2</sub>:

$$\text{O of silica combined with RO} = \frac{\left( \frac{2b}{7} \times k \right) (2b-2b')}{\frac{2b}{7}} = k \left( \frac{2b-2b'}{7} \right)$$

$$\text{O of silica combined with R}_2\text{O}_3 = \frac{2b}{7} k - k \left( \frac{2b-2b'}{7} \right) = k \times \frac{2b'}{7}$$

and formula is :

$$\left( \frac{2b-2b'}{7} \right) \text{ R. } k \left( \frac{2b-2b'}{7} \right) \text{ Si ; O of acid } k \left( \frac{2b-2b'}{7} \right) =$$

$$\begin{aligned} \text{O of bases } \left[ \frac{2b-2b'}{\gamma} \right] \times k \left[ \frac{2b'}{\gamma} \right] R_2, k \left[ \frac{2b'}{\gamma} \right] \text{Si;} \\ \text{O of acid } k \left[ \frac{2b'}{\gamma} \right] = \text{O of base } \left[ \frac{2b'}{\gamma} \right] \times k \end{aligned}$$

The silicates in RO and  $R_2O_3$  are of the same type as  $k \times O$  of base and of the same type as the compound itself.

We could prove in the same manner that if the weight  $b''$  of  $Al_2O_3$  were not equivalent for saturation of silica to that of the lime it replaces in the compound, the type of the silicate, the oxygen ratio, is changed, but remains the same for the silicates in RO and  $R_2O_3$  as the new ratio of the compound itself.

Hence: Let a slag be expressed with  $SiO_2$  or  $SiO_3$ , as the symbol for silica; let the equivalents or the atomic weights be used, the empirical or rational formulæ, the nomenclature neutral, e. g., sesquiacid, sesquibasic.....slag, or the more modern names derived from hypothetical radicals be employed; in all cases the oxygen ratio remains the same, as it should be. This ratio constitutes, so to speak, the individual feature of a silicate, it decides as to its greater or lesser fusibility, its possible coexistence with certain grades of iron, and, since the transformation of all the bases into their equivalent of lime does not modify it in any manner, as we have just seen, we possess, then, in this method an absolutely exact and easy mode of comparison of two slags. No notation or symbol of any kind is required; we have to deal only with *figures* representing the composition of the substance as given by the analysis itself; the relative character of two silicates can be judged at once, the tables of references furnishing all the other data pertaining to each case.

CALCULATION OF SLAG.—This method of transformation of all the constituents into lime will be found very advantageous in calculating a slag. It simplifies the work considerably, and from the beginning to the end the operations can be performed by a non-technical person without using any symbol or formula.



takes up 0.714 of silica, the 15.63 of lime in coal and ores will take up:  $0.714 \times 15.63 = 11.16\%$  of silica, leaving as *free silica* in the ore and coal  $22.52 - 11.16 = 11.36 \text{ SiO}_2$  to saturate with limestone. The 6% of *silica of the stone* will require, at the rate of 1.400 lbs. lime per lb. of  $\text{SiO}_2$ ,  $6 \times 1.40 = 8.40$  lime, leaving of *free lime* or the equivalent in the limestone,  $58.47 - 8.40$  or  $50.07$  *free lime*. We have to saturate in coal and ores, 11.36 free silica. At the rate of saturation adopted, it will take:  $11.36 \times 1.40$  lime = 15.91 lime; we have 50.07 free lime in 1 ton of limestone, we require only 15.91 of lime to *saturate the  $\text{SiO}_2$*  in coal and ores, hence, we need only *per ton of ore and  $\frac{3}{4}$  ton coal*,

$$\frac{15.91}{50.07} = 0.317$$

ton of stone. The charges are thus: 1 ton of ore, 0.75 ton of coal, 0.317 ton of limestone and, as the ore contains 50% of iron, we require:

$$\left. \begin{array}{l} 2 \text{ tons ore} \\ 1.50 \text{ tons coal} \\ 0.634 \text{ ton stone} \end{array} \right\} \text{ per ton of pig made.}$$

The composition of the slag is:

Silica in ore and coal per ton	}	22.520
of ore and per $\frac{3}{4}$ ton of coal		
In stone $6 \times 0.317$ ton		1.908
Total $\text{SiO}_2$		24.428
Lime in $\frac{3}{4}$ ton coal and 1 ton ore (per ton ore)		15.63
In stone $0.318 \text{ ton} \times 58.47\%$		18.59
Total lime		34.22

and composition of slag is:

$\text{SiO}_2 = 24.428$ or reducing to a	$\text{SiO}_2 = 41.66$
$\text{CaO} = 34.220$ percentage:	$\text{CaO} = 58.34$
<hr/>	<hr/>
58.648	100.00

exactly a *sesquibasic silicate*. See Table V.

Using the preceding charges of ores, stone and coal we should have every reason to expect a slag of the above composition or of one very close to it.

We have adopted  $1\frac{1}{2}$  ton coal per ton of pig. If it were found that this could be reduced it should be done and the slag would hardly be modified in general character by this charge. If greater accuracy were necessary the preceding calculations could be made over again with the *new charges* in coal; but, practically, it is absolutely useless, the ash of coal entering, as it may be seen, as a small percentage into the general composition. With inferior cokes or anthracite it becomes an important factor *not to be neglected but too often ignored*. Cokes with 15% of ash are not uncommon in certain localities.

As an example of the close coincidence between slags actually run from known calculated charges and the slag determined *a priori* we quote the following slag run in a furnace 60 feet high, 16 feet bosh, running on hot blast 850 to 900° F. Pressure of blast  $7\frac{1}{2}$  lbs., American furnace, anthracite coal. The analyses of materials were as follows :

	Ores.	Stone.	Coal.
SiO <sub>2</sub> .....	23.31	9.90	3.00
Al <sub>2</sub> O <sub>3</sub> .....	4.51	3.88	2.30
CaO .....	1.61	28.00	0.10
MgO.....	3.41	16.00	0.08
Alkalies.....	2.67	----	----
Mn <sub>3</sub> O <sub>4</sub> .....	traces	----	----
P <sub>2</sub> O <sub>5</sub> .....	0.31	----	----
S.....	0.08	----	----

Making the calculations proportionally to the quantity of the different materials charged, we find that the slag contained :

	Metallic Iron 46.46%.	New Jersey Dolomite.	Lehigh Summit.
Charges :	8cwt. 1q 0lb.	3cwt. 1q 14lbs.	5—1—0
	924 lbs.	378 lbs.	588 lbs.

	Ores.	Stone.	Coal.	Total.
Silica .....	215.38	37.42	17.64	270.44 lbs.
Alumina .....	41.67	14.66	13.52	69.85 "
Lime .....	14.90	105.84	0.59	121.33 "
Magnesia .....	31.50	60.48	0.47	92.45 "
Alkalies .....	24.67	----	----	24.67 "
Mang. oxide .....	Traces	----	----	----
Total weight of slag .....				578.74 lbs.

924 lbs. of ore gave in iron 425 lbs., the ores having 46.60% Fe. With such slag, of which the character was sesquibasic, a light grade of iron was to be expected, such pig as contains in an average 1.50% silicon or 3.20% silica corresponding, in 425 lbs. of pig iron, to 13.60 lbs. of silica, which, subtracted from the total silica which went to form slag and pig, leaves a balance of 256.84 lbs.  $\text{SiO}_2$  to be expected in slag. The composition of the slag was then :

Calculated.	Per Cent.	The analysis gave:
$\text{SiO}_2$ ..... 256.84	$\text{SiO}_2$ ..... 45.44	$\text{SiO}_2$ ..... 44.27
$\text{Al}_2\text{O}_3$ ..... 69.85	$\text{Al}_2\text{O}_3$ ..... 12.36	$\text{Al}_2\text{O}_3$ ..... 12.91
Lime ..... 121.33	$\text{CaO}$ ..... 21.40	$\text{CaO}$ ..... 20.00
$\text{MgO}$ ..... 92.45	$\text{MgO}$ ..... 16.36	$\text{MgO}$ ..... 16.50
Alkalies ..... 24.67	Alk ..... 4.40	Alkalies ..... 3.98
		Ox. of iron ..... 2.47
		$\text{MnO}$ ..... Traces
		S ..... 0.56
		100.69

This quantity of iron, 2.47% is not abnormal, but occurs in many slags. If we take it into consideration in calculating the slag we have  $99.96 + 2.40 = 102.36$ . Reducing to a percentage we find :

Calculated Slag (iron added).	Actual Analysis.
$\text{SiO}_2$ ..... 44.34	44.27
$\text{Al}_2\text{O}_3$ ..... 12.06	12.91
$\text{CaO}$ ..... 20.88	19.81
$\text{MgO}$ ..... 16.00	16.50
Alkalies ..... 4.22	3.98
Ox. iron ..... 2.47	2.47

The iron was found to be No. 3 light gray, containing 1.53 silicon. Transformed into lime, this slag corresponds to :

$\text{SiO}_2$ ..... 40.66
$\text{CaO}$ ..... 59.34
100.00

A typical sesquibasic slag has for its composition :

$\text{SiO}_2$ ..... 41.66
$\text{CaO}$ ..... 58.34
100.00

Table V.

But, if *we neglect* the 2.47% of iron *not taken into consideration in the first calculations* we find when transformed into lime :

SiO <sub>2</sub>	41.65	} for the composition of the "calculated slag."
CaO	58.36	

Having explained how to obtain the formulæ of slags with the symbols SiO<sub>2</sub> or SiO<sub>3</sub> for silica and how to transform the old formula into the new one or inversely, and possessing now, for all cases, an easy and rapid method of comparison of two slags, by transforming all the bases into lime, without using any chemical symbols, or making any hypotheses as to their composition, we shall proceed to the critical examination of a number of slags for which we know, at least and with certainty the grade of iron accompanying them, to see if the general statement that as the slag is more basic the tendency of the iron is to be of a darker grade, finds itself corroborated by blast furnace practice.

We give first the full analyses of the slags, as they were given by the different writers, or as they were obtained by us, many of them having been made by ourselves, completing them by a succinct description of the furnace from which they were run, and of the circumstances of their production as nearly as we have been able to ascertain them. For many slags we have also the analyses of the ores, stone and coals, and the charges, but they do not figure in this paper. In the transformation of the slags into lime, we have often stopped the operations at the first decimal; it is a sufficient approximation for a study of such compounds.

TABLE VI.—ANALYSES OF SLAGS.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
SiO <sub>2</sub> .....	46.37	45.28	38.48	43.40	70.23	53.79	49.57	48.39	41.11	37.84	45.64	41.11	39.95	40.30
Al <sub>2</sub> O <sub>3</sub> .....	4.30	14.30	15.13	12.30	6.37	13.04	9.00	6.66	13.45	13.30	10.84	9.46	17.41	16.45
CaO.....	38.64	32.09	32.92	18.13	30.41	25.67	10.22	10.22	29.52	20.68	35.01	37.60	29.64	30.00
MgO.....	3.78	7.44	7.44	4.50	2.70	0.57	15.15	10.22	4.75	2.93	3.16	2.11	6.47	7.39
MnO.....	1.86	1.02	1.62	5.80	2.70	2.30	25.84	33.96	0.66	0.80	traces.	1.61	0.91	0.84
FeO.....	0.95	3.03	0.76	10.99	0.15	2.44	0.04	0.06	Alk.	20.83	0.71	0.38	0.24	0.57
K <sub>2</sub> O.....	0.30	1.56	1.92	.....	.....	.....	.....	.....	Alk.	Alk.	Alk.	Alk.	Alk.	.....
Na <sub>2</sub> O.....	0.14	CaS <sub>2</sub>	Sulp. Ca	CaS <sub>2</sub>	.....	.....	.....	.....	1.84	1.06	0.82	0.71	1.46	1.30
S.....	0.08	1.87	2.22	8.97	.....	.....	.....	.....	S. Calc.	S. Calc.	S. Calc.	S. Calc.	S. Calc.	2.71
P <sub>2</sub> O <sub>5</sub> .....	traces.	.....	0.15	.....	.....	.....	.....	.....	1.34	1.77	8.30	6.41	3.60	traces.
Character of Iron.....	Gray	White.	Foun-	Gray.	Gray.	Mot-	Gray.	White.	White.	White.	Gray.	Gray	Gray	Gray
	No. 3.	.....	dry	.....	.....	tled.	.....	.....	.....	.....	.....	No. 2.	No. 2.	No. 2.
Bl. Furnaces.....	Edalen	Dowla	Gray	West-	Sweden	Sweden	Sweden	Spiegel-	English	English	English	English	English	English
	Sweden	land.	Eng-	phalia.	land.	land.	land.	eisen.	phalia.	phalia.	phalia.	phalia.	phalia.	phalia.

TABLE VI.—(Continued.)

	15	16	17	18	19	20	21	22	23	24	25	26	27	28
SiO <sub>2</sub> .....	41.64	42.94	36.80	48.42	29.25	37.80	40.10	40.50	37.99	38.36	39.30	39.71	49.57	47.39
Al <sub>2</sub> O <sub>3</sub> .....	13.30	16.29	13.80	7.56	19.25	13.70	10.40	9.90	14.33	9.28	11.28	18.96	9.00	6.56
CaO.....	35.91	31.10	46.00	27.89	38.25	48.50	49.80	49.50	47.66	39.50	43.84	35.36	.....	.....
MgO.....	4.21	4.16	2.54	6.48	0.60	.....	.....	.....	.....	.....	.....	0.66	15.15	10.22
MnO.....	0.74	0.51	.....	6.37	8.76	.....	.....	.....	.....	.....	.....	0.62	28.84	33.96
FeO.....	0.11	0.34	.....	4.39	1.04	.....	.....	.....	.....	.....	.....	0.897	0.04	0.06
K <sub>2</sub> O.....	Alk.	Alk.	Alk.	.....	.....	.....	.....	.....	.....	.....	.....	Alk.	.....	.....
Na <sub>2</sub> O.....	0.70	1.87	0.86	.....	.....	.....	.....	.....	.....	.....	.....	Cu 0.068	.....	.....
S.....	Ca. S.	Ca. S.	.....	.....	2.16	.....	.....	.....	.....	.....	.....	Ca. S.	0.80	.....
	2.19	2.16	.....	0.02	SiO <sub>2</sub>	.....	.....	.....	.....	.....	.....	2.35	.....	.....
P <sub>2</sub> O <sub>5</sub> .....	traces.	traces.	.....	.....	0.76	.....	.....	.....	.....	.....	.....	traces.	.....	.....
	Gray	Gray	Gray.	Gray.	Gray, 1.	Gray.	Gray.	Gray &	Gray.	Gray.	Gray &	Gray.	Gray.	White.
	No. 2.	No. 2.	Light	Light	2 to 3.	Besse-	Besse-	Mottled.	Besse-	Prus-	Mottled	Prus-	Gray.	White.
	Aber-	Aber-	and	and	Cleve-	ges.	ges.	Besse-	ges.	slan,	Prus-	slan,	Hamm.	Hamm.
	dare.	dare.	Mottled	Mottled	land.	Bel-	Bel-	Bel-	Bel-	West-	West-	West-	Hamm.	Hamm.
	English	English	Sweden	Sweden	Eng-	gium.	gium.	gium.	gium.	phalia.	phalia.	phalia.	phalia.	phalia.



TABLE VI.—(Continued.)

	29	30	31	32	33	34	35	36	37	38	39	40	41	42
SiO <sub>2</sub> .....	52.80	57.00	45.40	57.80	38.60	32.65	35.00	35.40	39.00	41.85	39.07	44.87	39.46	36.59
Al <sub>2</sub> O <sub>3</sub> .....	8.40	10.60	4.60	2.10	18.40	22.00	19.70	15.00	14.10	14.73	9.33	9.14	8.35	8.33
CaO.....	5.60	3.60	4.20	8.60	35.80	31.00	29.90	46.00	44.00	30.99	45.59	23.37	39.81	39.65
MgO.....	9.00	13.60	8.60	4.60	3.60	0	8.80	0.50	1.00	4.75	3.17	14.13	13.31	9.32
MnO.....	26.30	5.40	33.40	23.20	...	4.20	8.80	...	1.00	1.24	0.80	0.99	1.94	2.04
FeO.....	1.40	6.80	1.60	21.50	2.00	2.00	1.00	...	1.40	2.55	0.60	3.33	3.01	2.12
K <sub>2</sub> O.....	...	...	...	...	...	...	...	...	...	...	Alk	Alk	Alk	Alk
Na <sub>2</sub> O.....	...	...	...	...	...	...	...	...	...	...	0.23	3.50	3.37	1.62
S.....	...	0.02	...	...	1.00	...	...	1.80	1.20	Sulphate	0.40	0.58	0.75	...
P <sub>2</sub> O <sub>5</sub> .....	...	...	...	...	...	...	...	...	...	...	SiO <sub>2</sub>	...	...	...
	White.	Mottled	White.	Hamm.	Gray.	Scotch	Scotch	Scotch	Beesd.	Mottled	Gray	White.	White.	Gray.
	Muesen.	White.	Muesen.	White.	Terre-	Gray	Gray	Gray	ges.	and	No. 1 & 2	N. J.	N. J.	Ameri-
					noire,	No. 1.	Nos. 2	Graph-	Cinders	White.	Colora-	Ameri-	Ameri-	can.
					France.		to 4.	itic.	Gray.	Dowling	do, 1/4	can.	can.	
								Bel-		Eng-	Puddled			
								gium.		land.	Cinders			
											contain-			
											ing 10%			
											SiO <sub>2</sub> .			

TABLE VI.—(Continued.)

	43	44	45	46	47	48	49	50	51	52	53	54	55	56
SiO <sub>2</sub> .....	40.17	43.22	50.10	35.48	44.38	47.16	45.98	47.99	43.07	48.16	43.55	45.71	48.50	48.35
Al <sub>2</sub> O <sub>3</sub> .....	6.59	9.11	8.20	10.26	8.02	10.41	10.17	9.21	8.80	9.14	10.64	13.19	12.05	12.74
CaO.....	36.10	36.08	27.04	35.79	37.58	23.30	25.15	22.53	28.30	27.17	28.30	30.20	25.41	24.83
MgO.....	8.60	7.92	9.40	9.60	9.01	15.70	15.99	15.63	13.32	9.51	12.70	6.96	10.70	10.71
MnO.....	3.47	0.82	0.02	2.54	0.92	1.85	1.95	2.10	2.27	1.28	1.05	0.59	0.53	0.63
FeO.....	3.06	1.02	4.86	3.73	2.16	0.28	traces	traces	2.65	3.80	1.68	2.31	1.74	1.58
K <sub>2</sub> O.....	Alk	Alk	Alk	Alk	...	Alk	Alk	Alk	Alk	Alk	Alk	Alk	Alk	Alk
Na <sub>2</sub> O.....	1.02	1.79	...	1.94	...	0.98	0.64	1.57	1.05	0.60	2.00	1.38	0.35	0.34
K <sub>2</sub> O.....	0.39	0.59	...	0.46	0.45	0.45	0.28	0.12	0.64	0.41	...	...	0.58	0.52
P <sub>2</sub> O <sub>5</sub> .....	...	...	...	...	...	...	...	...	...	...	...	...	...	...
	Gray.	White	White.	White	Mottled	White.	White.	White.	Gray	White	Gray.	Light	White.	White
		Mottled		Chro-					No. 2.	and		Gray		and
				mium.						Mottled		No. 3.		Mottled

\*All American furnaces.

TABLE VI.—(Concluded.)

	57	58	59	60	61	62	63	64	65	66	67	68	69	70
SiO <sub>2</sub> .....	42.80	39.15	42.64	40.97	43.19	46.80	43.36	40.45	42.77	46.04	46.11	44.37	42.77	35.48
Al <sub>2</sub> O <sub>3</sub> .....	9.76	10.32	13.48	11.31	16.33	13.69	16.92	8.90	11.90	13.05	11.69	12.91	11.93	10.36
CaO.....	28.52	22.76	27.75	30.30	24.73	21.38	23.67	23.69	23.96	21.88	31.66	19.81	23.56	35.79
MgO.....	14.55	14.37	12.80	13.77	12.85	14.75	13.91	15.65	16.78	16.36	14.80	16.50	16.78	9.60
MnO.....	1.06	0.35	0.90	0.10	traces.	traces.	traces.	3.01	traces.	0.30	traces.	traces.	traces.	2.64
FeO.....	1.99	1.61	2.12	1.88	1.55	1.18	0.99	0.99	0.80	1.38	1.73	2.47	1.39	3.73
K <sub>2</sub> O.....	Alk.	Alk.	Alk.	Alk.	Alk.	Alk.	Alk.	Alk.	Alk.	Alk.	Alk.	Alk.	Alk.	Alk.
Na <sub>2</sub> O.....	0.60	0.79	0.13	0.79	0.69	1.66	0.50	1.13	3.44	1.66	2.91	3.48	3.44	1.94
S.....	0.73	0.75	0.90	0.88	0.66	0.51	0.68	0.68	0.64	0.54	0.55	0.56	0.57	0.46
P <sub>2</sub> O <sub>5</sub> .....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	Gray No. 1.
	Mottled	Gray No. 2.	Gray.	Gray No. 1.	Gray No. 2.	Gray No. 2 and 3.	Gray No. 3.	Gray No. 2.	Gray No. 2 and 3.	No. 3 and Mottled	Mottled	Gray No. 3. Light.	Gray No. 3.	Gray No. 1.

All American furnaces.

(1.) Edsken, Sweden.—Hot blast, 572° Farh.; height of furnace, 44' to 48'; boshes, 7'4"; blast, 0<sup>k</sup>.07 to 0<sup>k</sup>.105; average, 0.0875 ky. per □ centimetre = 1.20 lbs. per square inch; very fluid slag.

(2.) Dowlais furnace.—Ores, mixture of argillaceous carbonates and hematites; iron run; generally gray No. 2 and No. 3.

(3.) Dowlais furnace. (4.) Westphalia slag, leek green, the quantity of FeO, 10.99%, is remarkably high; vitreous and conchoidal fracture. (5.) Argillaceous ores, enamel like, bluish white, wood furnace, Sweden. (6.) Swedish furnace, wood as combustible, green and vitreous slag; spathic carbonates and brown hematites; air *very hot*. (7.) Spiegeleisen. (8.) Do. Spiegeleisen Swedish furnace. (9.) Hot blast, Dowlais. (10.) Cold blast, English. (11)–(12.) Argillaceous ores; pisolithic ores and puddle cinders. (13)–(14.) Aberdare B. furnaces, argillaceous ores, cold blast. (15)–(16.) Aberdare furnaces, hot blast 315° C. (17.) Coke furnace, Tonlaw. (18.) Lake and bog ores, cold air 0.07 kilo. per cm<sup>2</sup>, Tinspong, Sweden, charcoal furnace. (19.) Manganiferous ores containing 37.19% mang. oxide, Cleveland furnace. (20.) Bessèges, Belgium, hot blast 536° Farh.: pressure, 0<sup>m</sup>.12 to 0<sup>m</sup>.14. (21)–(22)–(23.) Do. (24)–(25.) Berge Borbeck furnace, hematites and argillaceous ores, poor; average, 35% iron; coke furnace, 47 ft. high x 15'6" boshes; crucible, 5'3" diam.; temperature of air, 180° C.; pressure, 0.16m. mercury per square centimetre. (26.) Austrian furnace, hematites and magnetites; hot blast; pressure, 0.069m. mercury; coke furnace, height 48'; boshes, 13'6"; hearth, 3'4"; temperature blast, 150°C.; pressure in lbs., 2½ to 3 lbs. (27.) Hamm furnace slag, manganiferous ores; manganese oxide in slag 25.84%. (28.) 33.96% MnO in slag. (29.) Müsen furnace, Spiegeleisen 26.20% MnO in slag. (30.) Müsen slag, 6.80 FeO in slag, 540 MnO. (31.) Do., Spiegeleisen MnO in slag 33.40%. (32.) Cold blast Hamm furnace, slag containing 29.20% MnO and 21.50 FeO. (33.) Terrenoire (France). (34.) Scotch iron. (35.) Do. (36)–(37.) Bessèges (Belgium) furnaces, 20% puddle cinders added to charges for slag, No. 37. (38.) English slag, Dowlais furnace; average. (39.) Slag from Colorado furnace; Hot Spring and Calumet ores, mixture of

rich magnetites 58% iron ; and rich hematites 45% iron ; Bessemer ores 25%, puddle cinders containing 9.47% titanitic acid added regularly to the charges. Iron No. 1 and No. 2 Foundry, very tough ; coke furnace 70 ft. high, 18% ashes.

(40.) Magnetite ores from New Jersey, very rich, general average, 50 to 55%. Iron, with gangue of free silica, hornblende, iron mica, furnace 45 feet high. Anthracite. Pressure of blast  $3\frac{1}{2}$  lbs. per square inch; temperature, 750 to 800° F. (41.) Same ores, with a mixture of one-half Staten Island hematite, containing 1.25% chromium, which went into the iron making it white and hard. (42.) Half Staten Island hematite, half New Jersey magnetites, chromium in the pig iron, 1.10%. (43.) All New Jersey magnetites. (44.) Do. (45.) Do. ; ores very silicious at the time, containing as much as 40% hornblende and iron mica, the furnace being only 45 feet high, they did not have time to be reduced, got into the hearth, fused and passed out as slag, which explains the anomaly of such an acid slag in connection with a gray forge iron. (46.) Staten Island hematites added to the charges, making the iron white; chromium in the iron, 1.20%. (47.) Regular N. J. hematites. (48)-(49)-(50.) Do. (51.) Same ores, but furnace 60 feet high ; pressure of blast, 6 to 7 lbs.; temperature, 800 to 900° Fahr. (52) to (70.) Do.

Average charges for Pig, 1.00.

Ores, 2.00. New Jersey magnetites generally.

Stone, 1.00. New Jersey dolomites.

Coal, 1.50. Lehigh anthracite and Scranton.

To compare these slags we have to transform them all into lime, and, as the approximations of a type to "basicity" is more logically expressed by the quantity of lime, we shall tabulate *only* the quantity of lime (calculated in some cases to only one decimal) to which all of the basic elements of the slags are equivalent. As some of the results fall between two types, the slag of the type to which it comes the nearest will determine the designation. An acid slag containing 31.80% CaO and the next type, the sesquiacid,

38.35% CaO ; (see tables) any slag which contains a quantity of lime greater than the average  $= \frac{38.35 + 31.81}{2} = 35.08\%$  of lime will be

tabulated as *sesquiacid*, if *less* as an *acid* slag. Any slag containing a quantity of lime greater than 43.31%, the average of 38.35 (sesquiacid) and 48.28 (neutral), will be tabulated as *neutral*, below this figure as *sesquiacid*. Any slag containing more than 53.31% CaO, the average of 48.28% (neutral) and 58.34% sesquibasic, will be tabulated as *sesquibasic*, below that figure as *neutral*. Any slag containing more than 61.73% CaO, the average of 58.34 neutral and 65.12 (bibasic), will be tabulated as *bibasic*, below this *sesquibasic*.

Any slag containing more than 69.42% CaO average of 65.12 (bibasic) and 73.70 (tribasic) will be tabulated as *tribasic*, below this as *bibasic*.

We give in a special column the amount of lime contained in each type, the figures being followed by capital letters, the first letters of the denomination of each type. Thus : A stands for acid, SA for sesquiacid, N for neutral, SB for sesquibasic, B for bibasic, T for tribasic.

In the next column we have put down the preceding figures, representing the *limit* of lime at which a slag has been classified under the type next in basicity. This was done in case of a possible approximation to one type, leaving in doubt the character of the slag ; but, as it will be noticed, it was not necessary in any case. Another column contains the character of the slag determined as explained. The next gives the character of the pig iron accompanying each slag, and the last contains such observations as may explain certain anomalies observed in the type in connection with the grade of iron, or such other special data regarding certain slags which make them rather abnormal. For details we refer to notes, pages 69 to 71, and to the Table VI., which gives the composition in full.

TABLE VII.

Nos. of Slags.	Equivalent of Lime in slag.	Lime in nearest type.	Limit of lime deciding type.	Character of Slags.	Character of Pig Iron Run.	OBSERVATIONS.
1	55.30	58.34 S. B.	53.31	Sesquibasic.	Gray, No. 3.	
2	57.37	58.34 S. B.	"	Sesquibasic.	White.	
3	65.00	65.12 B.	61.73	Bibasic.	Gray, No. 2.	
4	57.50	58.34 S. B.	53.31	Sesquibasic.	Gray.	10.90 FeO and 5.80 MnO in Slag.
5	32.00	31.81 A.	35.08	Acid.	Gray.	
6	48.00	48.28 N.	43.31	Neutral.	Mottled.	
7	53.00	58.34 S. B.	53.31	Sesquibasic.	Gray.	Very hot blast. MnO 25.84.
8	48.30	48.28 N.	43.31	Neutral.	White.	MnO 33.96. Spiegeleisen.
9	60.00	58.34 S. B.	53.31	Sesquibasic.	White.	Cold blast.
10	62.00	" S. B.	"	Sesquibasic.	White.	
11	56.00	" S. B.	"	Sesquibasic.	Gray.	Puddle cinders in the charges.
12	59.00	" S. B.	"	Sesquibasic.	Gray.	" " "
13	63.30	65.12 B.	61.73	Bibasic.	Gray, No. 1.	
14	64.00	" B.	"	Bibasic.	Gray, No. 2.	
15	61.80	" B.	"	Bibasic.	Gray, No. 2.	
16	61.00	" B.	"	Bibasic.	Gray, No. 2.	
17	66.30	" B.	"	Bibasic.	Gray.	
18	54.40	58.34 S. B.	53.31	Sesquibasic.	Light gray. Mottled.	MnO = 6.37; FeO = 4.39. Cold blast.
19	72.50	73.70 T.	69.42	Tribasic.	Gray, No. 1.	MnO; 8.76.
20	65.20	65.12 B.	61.73	Bibasic.	Gray.	
21	62.20	" B.	"	Bibasic.	Gray and mottled.	
22	61.90	" B.	"	Bibasic.	Mottled and gray.	
23	65.10	" B.	"	Bibasic.	Gray.	
24	58.80	58.34 S. B.	53.31	Sesquibasic.	Gray forge. M.	
25	61.30	" S. B.	"	Sesquibasic.	Gray forge.	
26	63.50	65.12 B.	61.73	Bibasic.	Gray.	
27	51.30	58.34 S. B.	53.31	Sesquibasic.	Gray.	MnO 25.84%.
28	53.00	" S. B.	"	Sesquibasic.	White.	MnO 33.96.
29	46.40	48.28 N.	43.31	Neutral.	White.	MnO 29.30.
30	47.70	" N.	"	Neutral.	White.	MnO 5.46%; FeO 6.80.
31	46.50	" N.	"	Neutral.	White.	MnO 33.40.
32	58.37	58.34 S. B.	53.31	Sesquibasic.	White.	MnO 29.30; FeO 21.50.
33	67.00	65.12 B.	61.73	Bibasic.	Gray, No. 1.	
34	69.50	73.72 T. B.	69.42	Tribasic.	Scotch gray, No. 1.	
35	66.50	65.12 B.	61.73	Bibasic.	Scotch gray, No. 2.	
36	66.40	" B.	"	Bibasic.	Gray, No. 1.	Graphitic Iron.
37	66.40	" B.	"	Bibasic.	Gray, No. 1 and No. 2x	
38	60.00	58.34 S. B.	53.31	Sesquibasic.	White and mottled.	
39	63.07	65.12 B.	61.73	Bibasic.	Gray, Nos. 1 and 2.	¼ Puddled cinder containing 9.47 SiO <sub>2</sub> .
40	58.80	58.34 S. B.	53.31	Sesquibasic.	White.	
41	63.16	65.12 B.	61.73	Bibasic.	White.	¼ Staten Island Hematite. Chromium in iron making it white.
42	65.00	" B.	"	Bibasic.	White.	¼ Staten Island Hematite. 1.25 Chrom. in iron making it white.
43	62.00	" B.	"	Bibasic.	Gray.	
44	60.00	58.34 S. B.	53.31	Sesquibasic.	White.	
45	53.30	" S. B.	"	Sesquibasic.	Gray forge.	45% Silicates of iron Hornblende and Mica in ore not reduced and increasing unduly SiO <sub>2</sub> .
46	65.00	65.12 B.	61.73	Bibasic.	White.	¼ Staten Island Hematite. Chromium in iron.
47	59.70	58.34 S. B.	53.31	Sesquibasic.	White.	
48	57.70	" S. B.	"	Sesquibasic.	White.	
49	58.00	" S. B.	"	Sesquibasic.	White.	
50	56.40	" S. B.	"	Sesquibasic.	White.	
51	60.40	" S. B.	"	Sesquibasic.	Gray, No. 2.	
52	56.10	" S. B.	"	Sesquibasic.	White and mottled.	
53	61.80	65.12 B.	61.73	Bibasic.	Gray.	
54	58.70	58.34 S. B.	53.31	Sesquibasic.	Light gray forge.	
55	56.30	" S. B.	"	Sesquibasic.	Mottled and white.	
56	56.20	" S. B.	"	Sesquibasic.	Mottled.	
57	60.30	" S. B.	"	Sesquibasic.	Mottled.	
58	64.60	65.12 B.	61.73	Bibasic.	Gray, No. 2 and No. 3.	
59	63.00	" B.	"	Bibasic.	Gray.	
60	64.10	" B.	"	Bibasic.	Gray, No. 2xx.	
61	62.35	" B.	"	Bibasic.	Gray, No. 2.	
62	57.90	58.34 S. B.	53.31	Sesquibasic.	Gray.	
63	62.30	65.12 B.	61.73	Bibasic.	Gray, No. 3.	
64	63.50	" B.	"	Bibasic.	Gray, No. 2.	
65	61.80	" B.	"	Bibasic.	Gray, No. 3.	
66	59.20	58.34 S. B.	53.31	Sesquibasic.	No. 3 and Mottled.	
67	58.50	" S. B.	"	Sesquibasic.	Mottled.	
68	60.00	" S. B.	"	Sesquibasic.	No. 3, Gray.	
69	61.80	65.12 B.	61.73	Bibasic.	No. 3, Gray dark.	
70	66.30	" B.	"	Bibasic.	Gray, No. 1.	

Referring to the data contained in the preceding table we see that :

When the slags were "*neutral*," which happened five times, the iron was four times white and once mottled.

When they were "*sesquibasic*," which happened 32 times, the iron was twelve times white ; three times white and mottled ; four times mottled ; twice light gray and mottled, and eleven times gray ; the shades of gray being mostly light.

When they were "*bibasic*," which happened 30 times, the iron was three times white ; twice gray and mottled gray, and 25 times gray, graphitic No. 1, No. 2<sup>xx</sup>, No. 2<sup>x</sup> and No. 2, the darker shades corresponding most generally to slags reaching very near the typical bibasic slag or even going beyond it in quantity of lime. *The three cases* when the iron was "white" it was due invariably to the presence of chromium in the pig ; chromium making the pig iron white and hard when present in certain quantities ; the conditions of the furnace were not normal so far as the study of types of slags is concerned.

When they were "*tribasic*," which happened twice, the iron was No. 1 graphitic iron.

When they were "*acid*," which happened once, the iron was gray.

We are justified in concluding at least from the examples quoted, that, with a neutral slag the iron can be expected to be normally white, exceptionally mottled.

With a slag approaching a sesquibasic slag, according to the conditions of the furnace, height, temperature and pressure of blast, the iron can be expected to affect the lightest grades of gray or to be mottled, being white only in special conditions, and a darker gray if the composition of the slag is decidedly sesquibasic. Irons run with such slags are very advantageous as forge irons. The pig contains a greater percentage of iron and less silicon and carbon than grayer pigs, conditions very favorable in the puddling process, which is intended to eliminate all substances foreign to the iron.

With a bibasic slag, in normal conditions of ores and charges, we can expect invariably a gray pig from the darkest shades to

No. 2. No. 1, No. 2<sup>xx</sup> and kish cinders, if the composition in lime reaches over the type of bibasic No. 2<sup>x</sup> and No. 2, if not quite up to the percentage of lime of the latter, as the case may be.

With a tribasic slag the iron will invariably be a No. 1 iron, Scotch gray (judging from the limited number of examples of such slags, which are not very economical).

An acid slag, as could be expected from diminished fusibility when the proportion of silica goes above a certain limit, corresponds to gray iron.

The higher grades of iron contain the most silicas and carbon (total carbon), corresponding therefore to higher temperatures in a furnace, a condition necessary to insure the reduction of the silica and the passage of silica into the pig, as well as the solution of the carbon in the molten iron; they are accompanied by the more basic slags. Blast furnace practice corroborates then completely the direct experiments on the fusibility of silicates which showed that the more basic they are the less their fusibility, and that, beyond a certain limit of acid, the silicates become again more refractory.

If objections are made to the denomination "Basic," "Bibasic," "Neutral," slags used in this discussion, we can say: Putting aside all considerations as to the molecular constitution of silicates and taking only as a guide *the oxygen ratio, an element of comparison which the analysis furnishes in all cases.*

The silicates in which the ratio of oxygen of  $\text{SiO}_2$  to oxygen of the bases is comprised between  $\overset{\text{(Sesquibasic.)}}{4 : 3}$  and  $\overset{\text{(Bibasic.)}}{4 : 4}$  (1 : 1) accompany most invariably the higher grades of iron; when this ratio falls between 4 : 2 (neutral 2 : 1) and 4 : 3 (sesquibasic), mottled iron and lighter grades of gray may be expected, darker as the ratio approaches 4 : 3.

At 4 : 2 (2 : 1), white iron and occasionally mottled iron can be depended upon. When this ratio reaches 1 : 4 (acid), the fusibility appears to diminish again, and as a consequence, the darkest grades are obtained.

At 4 : 6 (2 : 3) (tribasic) graphitic iron and kish cinder are the



rule. If these deductions are correct, and the more numerous the observations the better their truth could be ascertained, their importance is not to be overlooked. The failure to obtain a certain grade of iron with a given slag within certain limits would then be a warning to an intelligent iron master to look in his ores or other materials charged in the furnace, for a disturbing element or for abnormal conditions of temperature, volume and pressure of blast. It would call for a thorough chemical analysis. The same ores frequently change in composition. When silica is present in a combined state in an iron ore, as hornblende or iron mica, these silicates of iron may melt before being reduced, especially in a low furnace, and pass out in the slag *as such*, and unreduced completely changing *its character* as calculated from a "general analysis," or "expected" from a previous practice with the same ores. Such a circumstance did present itself in one of the slags quoted, No. 45. It showed at the analysis 50.10 silica and 4.88 FeO, corresponding, transformed into lime, to a slag containing 53.20 CaO, just about the limit, 53.31, to be called a sesquibasic slag (58.34); it was tabulated so, but, strictly speaking, it was nearer a neutral slag, 48.28. With such a slag an iron of lighter gray than gray forge iron was to be expected. If a darker one was obtained, it was certainly due to the fact that, omitting the *silicate of iron* melted without reduction in a low furnace, and existing simply as an *inert matter* in the liquid slag, the slag had a different saturation for silica than the apparent one. A more complete and thorough examination of the slags quoted would disclose for several of them other anomalies, more or less important, but it would carry us too far. We have intended to show, only in a general manner, that the relation between the chemical character of a slag and grade of iron is much closer than, we believe, it is generally admitted to be, leaving far more complete and numerous observations to determine the question, not forgetting the wise maxims of Sir Lowthian Bell and his reserve: "If it is proper to give an opinion on a subject which one has not *thoroughly* experimented."

The following Tables VIII. and IX. recapitulate practically the results of this examination. No formulæ or symbols are used in

it; the bases being called by the names they are generally known by. It is, so to speak, a practical table allowing any one not familiar with technical chemistry to transform a slag of any composition into lime and also to find the oxygen ratio if desired. Comparing the results with those tabulated, the character of the slag can be ascertained and permit its fusibility and the iron "likely" to be expected in normal conditions of furnace, as well as its relation with another one. The Table IX. of equivalence includes all the bases likely to be met with in slags, some as constant elements, others as occasional ones in certain localities. Table VIII. giving also the saturation of lime for silica, or inversely, for different types of slags of different fusibility these figures can readily be used, as explained previously, for the calculation, *a priori*, of a slag from certain charges in ores, stone and coal of which the analyses may be given:

TABLE VIII.—TYPES OF SLAGS (*Resumé*).

Chem. Denomination: <i>Acid.</i> Disilicates.	Chem. Denomination: <i>Segregated.</i> Trisilicates.	Chem. Denomination: <i>Neutral.</i> Metasilic Monosilicates.	Chem. Denomination: <i>Segregated.</i> Disilicates.	Chem. Denomination: <i>Basic.</i> Orthosilic Monosilicates.	Chem. Denomination: <i>Tri-basic.</i> Parasilic Monosilicates.
Oxygen Ratio: O of Silica: O of Bases 4 : 1	Oxygen Ratio: O of Silica: O of bases 3 : 1	Oxygen Ratio: O of Silica: O of bases 2 : 1	Oxygen Ratio: O of Silica: O of bases 4 : 3	Oxygen Ratio: O of Silica: O of bases 1 : 1	Oxygen Ratio: O of Silica: O of bases 2 : 3
Composition: Silica ..... 68.19 Lime ..... 31.81	Composition: Silica ..... 61.65 Lime ..... 38.35	Composition: Silica ..... 51.72 Lime ..... 48.28	Composition: Silica ..... 41.66 Lime ..... 58.34	Composition: Silica ..... 34.88 Lime ..... 65.12	Composition: Silica ..... 24.90 Lime ..... 75.10
Saturation: 1 Lime-satur. 2.143 Silica 1 Silica saturates. .... 0.466 Lime	Saturation: 1 Lime ..... 1.607 Silica 1 Silica ..... 0.622 Lime	Saturation: 1 Lime ..... 1.071 Silica 1 Silica ..... 0.932 Lime	Saturation: 1 Lime ..... 0.714 Silica 1 Silica ..... 1.400 Lime	Saturation: 1 Lime ..... 0.538 Silica 1 Silica ..... 1.858 Lime	Saturation: 1 Lime ..... 0.357 Silica 1 Silica ..... 2.859 Lime
Fusibility: "Fusible."	Fusibility: "Moderately Fusible."	Fusibility: "Very fusible."	Fusibility: "Very fusible," but less than preceding one.	Fusibility: "Fusible."	Fusibility: "Fusible," but less than preceding one.
Grade of iron likely to accompany such slag: Gray No. 2.	Grade of iron likely to accompany such slag: Gray, lighter.	Grade of iron likely to accompany such slag: White.	Grade of iron likely to accompany such slag: Mottled and Lighter Grays.	Grade of iron likely to accompany such slag: Gray No. 2, No. 2x, No. 2xx, and No. 1 occasionally.	Grade of iron likely to accompany such slag: Gray No. 1. Kish Cinder.

TABLE IX.

Bases likely to be found in slags.

Equivalence in Lime.		Oxygen in 1 lb. of Base.
1 lb. Alumina	= 1.631 Lime	0.466
1 lb. Magnesia	= 1.400 "	0.400
1 lb. Potash	= 0.594 "	0.170
1 lb. Soda	= 0.903 "	0.258
1 lb. Iron Oxide (FeO)	= 0.780 "	0.222
1 lb. Manganese Oxide (MnO)	= 0.780	0.225
1 lb. Baryta	= 0.365	0.104
1 lb. Copper Oxide (CuO)	= 0.704	0.201
1 lb. Lithia	= 1.866	0.550
1 lb. Nickel Oxide (NiO)	= 0.747	0.213
1 lb. Iron Sesquioxide (Fe <sub>2</sub> O <sub>3</sub> )	= 1.050	0.300
1 lb. Chromium Sesquioxide (Cr <sub>2</sub> O <sub>3</sub> )	= 1.100	0.314
Iron and Chromium Sesquioxide, (Ferric and Chromic oxide,) to be treated as Alumina.		O of Silica: 0.533

## SYNTHESES IN THE SUGAR GROUP.

BY EMIL FISCHER.\*

Translated by L. H. FRIEDBURG, Ph. D.

Until quite recently the sugars of the formula,  $C_6H_{12}O_6$ , were considered as the simplest members of the group. As long as the synthesis had not been applied products of animal and vegetable life were the only sources for the small number of sugars. In 1886 we knew four sugars of the formula  $C_6H_{12}O_6$ , viz.:

Grape sugar, or glucose.  
Fruit sugar, or laevulose.  
Galactose.  
Sorbinose.

Closely connected with these is arabinose which Scheibler, its discoverer, held to be an isomere of glucose, while Kiliani<sup>1</sup> in 1887 characterized it as a compound,  $C_6H_{10}O_6$ . A few other substances had in former times been erroneously incorporated into the sugar series. Of these inosite and dambose, which are identical, have been recognised by Maquenne<sup>2</sup> as derivatives of hexamethylene, while others, such as phlorose<sup>3</sup>, corcose<sup>3</sup> and cerebrose<sup>4</sup> are no longer considered as being chemical individuals.

Of the four remaining sugars the rare sorbinose has been but sparingly examined. According to the latest communications of Kiliani and Scheibler<sup>5</sup> it seems to have the same constitution as laevulose.

\* *Ber. d. Chem. Ges.*, **23**, 2114 (Abstract.)

<sup>1</sup> *Ber. d. Chem. Ges.*, **20**, 339.

<sup>2</sup> *Compt. rend.*, **104**.

<sup>3</sup> *Ber. d. Chem. Ges.*, **21**, 388.

<sup>4</sup> *Thierfelder, Zeitschr. für physiol. Chem.*, **14**, 209.

<sup>5</sup> *Ber. d. Chem. Ges.*, **21**, 3276.

On the other hand the structure of the three other important sugars ~~was~~ essentially known before my own researches began.

The formulæ now in use for glucose and galactose :

$\text{CH}_2(\text{OH}). \text{CH}(\text{OH}). \text{CH}(\text{OH}). \text{CH}(\text{OH}). \text{CH}(\text{OH}). \text{COH};$   
and for laevulose :

$\text{CH}_2(\text{OH}). \text{CH}(\text{OH}). \text{CH}(\text{OH}). \text{CH}(\text{OH}). \text{CO}. \text{CH}_2(\text{OH})$  are derived from the following facts :

Sodium amalgam changes glucose and laevulose into mannite ; while galactose under the same conditions furnishes dulcite. But mannite and dulcite are to be considered as the hexatomic alcohols of normal hexane, because they are able to take up six acetyl groups and to furnish normal hexyl iodide with hydriodic acid. Furthermore glucose and galactose when subjected to moderate oxidation by means of chlorine or bromine water yield the monobasic gluconic and galactonic acids and, on continued oxidation, the bibasic saccharic and mucic acids. They consequently contain the aldehydic group.

Zincke<sup>6</sup> and V. Meyer<sup>7</sup> objected to this conclusion, upon the basis that ketones also with the group  $\text{CO}. \text{CH}_2(\text{OH})$ , as for instance acetylcarbinol, may be transformed into oxyacids. This objection is not justified, because the formation of gluconic and galactonic acids takes place in acid solution, while the transition of acetylcarbinol into lactic acid has been effected only by alkaline oxidizers. In this latter case the carbinol may at first be transformed into the aldehyde, methylglyoxal, which then, under the influence of alkali must at once change to lactic acid.

Unlike the two aldehydes, laevulose is but very slowly attacked by cold bromine water and under the influence of more severe oxidizers it decomposes into products less rich in carbon<sup>8</sup>.

All three sugars combine like the ordinary aldehydes or ketones with hydrocyanic acid. By saponification of the cyanhydrines formed, three different acids,  $\text{C}_7\text{H}_{14}\text{O}_8$ , are produced which are changed into heptylic acids when boiled with hydriodic acid.

<sup>6</sup> *Ber. d. Chem. Ges.*, **23**, 636 and *Ann. Chem. (Liebig)*, **216**, 318.

<sup>7</sup> *Ber. d. Chem. Ges.*, **23**, 2344.

<sup>8</sup> *Kiliani, Ann. Chem. (Liebig)*, **205** 175.

Under these conditions glucose and galactose furnish normal heptylic acid, while laevulose is transformed into methylbutyl-acetic acid.

This method devised by Kiliani<sup>9</sup>, I consider to mark the greatest progress in the study of the sugar group during several decades. By its aid the old formula for glucose was confirmed and the ketonic formula given above for laevulose put beyond ambiguity. In the same manner Kiliani found the structure of arabinose<sup>10</sup> to be  $\text{CH}_2(\text{OH}). \text{CH}(\text{OH}). \text{CH}(\text{OH}). \text{CH}(\text{OH}). \text{COH}$ .

The addition of hydrocyanic acid implies the first successful step toward synthesis of compounds richer in carbon out of natural sugars.

Another support for the formula of glucose and galactose has been found recently in the observation that they form hydrazones<sup>11</sup> and oximes<sup>12</sup> just as the simple aldehydes do.

The only objection against the aldehyde formula which is maintained up to date, concerns the indifference of sugars towards fuchsine-sulphurous acid<sup>13</sup>. But this objection loses its importance if we consider that heretofore no simple oxyaldehyde of the fatty series has been tested by this reagent. For the time being it seems therefore not justifiable to replace the aldehyde formula by any other, especially as it explains all simple metamorphoses of the two compounds.

Thus the formulæ for the three kinds of sugar are derived from observations seemingly ample enough to serve as a basis for syntheses. But it was different in regard to the methods which were in use for the recognition and isolation of these compounds. Whosoever has tried to obtain glucose or laevulose in a pure state, from salt solutions only, by the methods formerly in use, will agree that it is quite impossible in that way to isolate such an artificial product from a mixture with other organic compounds and to characterize it as a chemical individual.

This want of suitable methods I experienced vividly myself

<sup>9</sup> *Ber. d. Chem. Ges.*, **18**, 3066 ; **19**, 221, 767, 1128.

<sup>10</sup> *Ber. d. Chem. Ges.*, **20**, 339.

<sup>11</sup> *Fischer, Ber. d. Chem. Ges.*, **20**, 824.

<sup>12</sup> *Rischbieth, Ber. d. Chem. Ges.*, **20**, 2673.

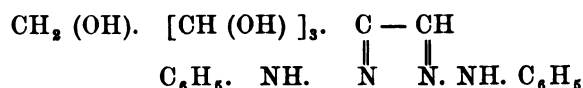
<sup>13</sup> *V. Meyer, Ber. d. Chem. Ges.*, **18**, 2343.

when seven years ago I attempted *for the first time the synthesis of a sugar* from the bromine compound of acroleine. At that time I obtained by decomposition of the bromide with baryta water a syrup which showed the ordinary sugar reactions. But all endeavors to obtain a pure preparation from the raw product were without success. Only four years later this was obtained after a useful agent for this purpose had been found in phenylhydrazin<sup>14</sup>.

The reaction between this base and sugars is easily shown as follows: Adding to a warm aqueous ten per cent. solution of glucose, a solution of phenylhydrazin in dilute acetic acid, the mixture at once assumes a yellow color. Heating on the water bath leads in ten or fifteen minutes to a deposit of fine yellow needles, which finally fill the entire liquid like a pulp. These needles have the composition  $C_{18}H_{22}N_4O_4$ , and are called glucosazone. They are formed by combination of one molecule of sugar and two of phenylhydrazin.

But the formation of this substance takes place in two phases.<sup>15</sup> At first, the sugar combines, like common aldehydes, with one molecule of the base to an hydrazone of the formula:  $CH_2(OH). [CH(OH)]_3. *CH(OH). CH : N. NH. C_6H_5$ .

This compound is easily soluble in water and consequently passes unnoticed in the experiment. On heating this hydrazone with an excess of hydrazin, it suffers a peculiar oxidation. The alcoholic group marked \* in the above formula, is transitorily changed into a carbonyl group which latter then fixes in known manner a second molecule of phenylhydrazin. Thus the glucosazone results, the structure of which is given by the formula:



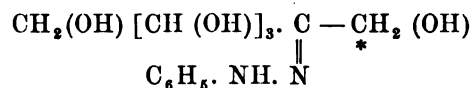
We are forced to look at the reaction in this way by the behavior of laevulose, which permits the entrance of the hydrazin groups in an inverted sequence. In this case also the first step

<sup>14</sup> Ber.d. Chem. Ges., 17, 579.

<sup>15</sup> Ber.d. Chem. Ges., 20, 822.



consists in the formation of an hydrazone easily soluble in water and non-crystallizable.



Then again the alcoholic group marked \* becomes oxidized, a second molecule of phenylhydrazine enters and allows the formation of a glucosazone identical with the one obtained from glucose.

The same reaction is shown by all natural sugars which reduce Fehling's solution, including lactose and maltose. It also obtains for the artificial sugars, or generally speaking, for all aldehydes and ketones which in neighboring position contain an oxidizable alcoholic group, that is, a primary or secondary alcoholic group.

The hydrazones of natural sugars are generally easily soluble in water; this is true for glucose, laevulose, galactose, sorbinose, lactose, maltose, arabinose, xylose and rhamnose.

Mannose<sup>16</sup> forms an exception. Its phenylhydrazone is very difficultly soluble in water, consequently it is precipitated from a cold solution of the sugar upon addition of phenylhydrazin acetate. Using a 10 per cent. mannose solution, a separation of almost colorless, fine crystals begins within one to two minutes and soon the entire liquid is filled with them. The optical isomeres of mannose behave similarly, as do also different artificially obtained sugars with seven, eight and nine carbon atoms.

Here the precipitation of the hydrazone is by far the best means for the recognition as well as for isolation and purification of the sugar, since this latter may easily be regenerated from its hydrazone by splitting this with hydrochloric acid in the following way. To finely pulverized mannose phenylhydrazone add four times its quantity of fuming HCl of Sp. Gr. 1.19 at ordinary temperature. On vigorously shaking, a clear brown liquid is rapidly obtained, the hydrochloride forming. After 1 to 2 minutes the splitting of the hydrazone becomes noticeable, since the crystallization of phenylhydrazine hydrochloride begins. In 10 to 15 minutes the reaction is completed and then the separation of the sugar from the filtered liquid offers no difficulty.

<sup>16</sup> *Ber. d. Chem. Ges.*, **20**, 832; **21**, 1805.

The osazones, which are almost insoluble in water, have proved to be still more valuable for the development of work in the sugar group. They crystallize with comparative ease and precipitate even from most dilute solutions. In addition, they differ in solubility, melting point and in optical behavior, and they are now consequently used for recognizing natural sugars.

The derivatives of these latter, as well as the important marks of difference are put down in the following table :

*Glucosazone*,  $C_{18}H_{22}N_4O_4$ . Is formed from glucose, laevulose, mannose, glucosamine and isoglucosamine. Almost insoluble in water, difficultly soluble in hot alcohol. Melting point near  $205^{\circ}C$ . The solution in glacial acetic acid turns the plane of polarization to the left.

*Galactosazone*,  $C_{18}H_{22}N_4O_4$ . From galactose. Almost insoluble in water, a little more soluble in alcohol than the preceding. Melting point near  $193^{\circ}C$ . No noticeable action on polarized light when dissolved in glacial acetic acid.

*Sorbinosazone*,  $C_{18}H_{22}N_4O_4$ . From sorbinose. Almost insoluble in water, easily soluble in hot alcohol. Melting point  $164^{\circ}C$ .

*Lactosazone*,  $C_{24}H_{32}N_4O_9$ . From lactose. Soluble in 80 to 90 parts of hot water. Melting point near  $200^{\circ}C$ . Dilute sulphuric acid changes it into its anhydride  $C_{24}H_{30}N_4O_8$ , which is almost insoluble in water.

*Maltosazone*,  $C_{24}H_{32}N_4O_9$ . From maltose. Soluble in about 75 parts of hot water. Melting point near  $206^{\circ}C$ . Does not furnish an anhydride.

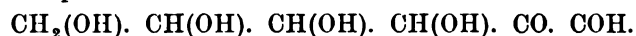
*Arabinosazone*,  $C_{17}H_{20}N_4O_3$ . From arabinose. Sparingly soluble in hot water, easily soluble in hot alcohol. Melting points near  $160^{\circ}C$ . Its alcoholic solution shows no action upon the polarized light.

*Xylosazone*,  $C_{17}H_{20}N_4O_3$ . From xylose. Deceptively similar to arabinosazone, but, in alcoholic solution strongly turns polarized light to the left.

*Rhamnosazone*,  $C_{18}H_{32}N_4O_3$ . From rhamnose (isodulcitol). Almost insoluble in water, easily soluble in hot alcohol. Melting point near  $180^{\circ}C$ .



tions for a successful operation. To finely powdered glucosazone the tenfold quantity of fuming HCl is added. It turns dark red, and a portion goes into solution with the same tint. It is thus transformed into its hydrochloride, which, however, is decomposed by water. If the mixture is rapidly heated to 40° C. and vigorously shaken a clear solution is obtained. This is kept for but one minute at 40° C. and then cooled down to 25° C. Now an ample crystallization of phenylhydrazine hydrochloride sets in which indicates the splitting of the osazone. At the same time the dark red tint of the liquid turns to a dark brown. In ten minutes the reaction is finished. The filtered liquid is freed from HCl and the glucosone is precipitated as an insoluble lead compound. It has not, so far, been made to crystallize, and, consequently, could not be analyzed, but its reactions, which correspond absolutely to those of glyoxal and with 1, 2-diketones, do not leave any doubt, that the compound is the aldehyde of fruit sugar and possesses the formula :



The behavior towards phenylhydrazine is particularly characteristic. The cold aqueous solution upon addition of phenylhydrazine acetate becomes rapidly turbid, and in five to ten minutes a dense precipitate of glucosazone is formed.

The glucosone combines also with aromatic orthodiamines and forms well-crystallizing chinoxaline derivatives. Finally its transformation by means of nascent hydrogen is particularly interesting, since heating with zinc dust and acetic acid changes it entirely into fruit sugar.

This method thus leads from grape sugar by way of the osazone and osone to fruit sugar and it is to be expected that in this manner most of the still unknown ketone sugars will be prepared from all aldehyde sugars. If we want to return from the ketone sugars to the aldehyde sugars we have to go by way of the alcohol. Considering the last example, the transformation would be as follows: Fruit sugar is easily reduced to mannite by means of sodium amalgam. Careful oxidation with nitric acid forms out of this its aldehyde, the mannose, and further, from this, as I shall show, grape sugar.

In studying the sugars the osazones are capable of application to other purposes.

The formulæ  $C_6H_{12}O_6$ ;  $C_6H_{10}O_5$ ;  $C_7H_{14}O_7$ , etc., showing the same percentage composition, the analysis alone of these sugars will never allow to decide in regard to the number of carbon atoms; we are therefore forced to analyze a derivative. For this purpose the osazones are best fitted since, as a rule, they may be obtained in a very pure state. They have been utilized so far for the determination of the empirical formulæ of arabinose<sup>20</sup>, sorbine<sup>21</sup> and xylose<sup>22</sup>.

In still other cases the osazones offer a new means of determining the constitution of a sugar. In former times rhamnose (isodulcite) was considered to be a hexatomic alcohol and an analogue of mannite, although its reducing action upon alkaline copper sol. was known. But the use of the hydrazin test showed, in furnishing<sup>23</sup> an osazone,  $C_6H_{10}O_3(N_2H.C_6H_5)_2$ , that the anhydrous rhamnose is a sugar of the formula  $C_6H_{12}O_5$ , for which later on the structural formula was found<sup>24</sup> to be  $CH_3.CH(OH).CH(OH).CH(OH).CH(OH).COH$ .

Another example is offered by milk sugar, which, as we know, is an anhydride of equal molecules of glucose and galactose. Its faculty of forming an osazone proves that it still contains one group— $CH(OH).COH$ . Since, furthermore, the osone which is formed from the osazone decomposes into galactose and glucosone when boiled with dilute acids, it follows that we find in sugar of milk the unchanged aldehydic group of the glucose molecule.<sup>25</sup>

This conclusion, which has been corroborated by the preparation of lactobionic acid<sup>26</sup> and by the hydrolysis of this latter, has led to a new conception of the constitution of milk sugar and of the closely related maltose.

Finally the hydrazones and osazones proved to be particularly valuable for the discovery of new sugars and of substances similar to sugars. These latter are obtained in a comparatively easy manner by moderate oxidation by polyatomic alcohols. As far as I know, it was Carlet<sup>27</sup> who made the first observation of this kind.

<sup>20</sup> Kiliani, *Ber. d. Chem. Ges.*, **20**, 345.

<sup>21</sup> E. Fischer, *Ber. d. Chem. Ges.*, **20**, 827.

<sup>22</sup> Tollens und Wheeler, *Ann. Chem. (Liebig)*, **254**, 315.

<sup>23</sup> Fischer und Tafel, *Ber. d. Chem. Ges.*, **20**, 1091.

<sup>24</sup> Fischer und Tafel, *Ber. d. Chem. Ges.*, **21**, 2173; see also Maquenne, *Compt. Rend.*, **109**, 603.

<sup>25</sup> Fischer, *Ber. d. Chem. Ges.*, **21**, 2643.

<sup>26</sup> Fischer und Meyer, *Ber. d. Chem. Ges.*, **22**, 361.

<sup>27</sup> *Jahresbericht für Chemie* (1860), 250.

(To be continued.)

## ABSTRACTS.

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### GENERAL CHEMISTRY.

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#### Combustion under High Pressure. W. HEMPEL.

It is a known fact, that the combustion of sulphur furnishes noticeable quantities of sulphuric anhydride along with sulphur dioxide. Also that hydrogen, illuminating gas or carbon when burned, allows the formation of nitrous acid easily to be shown. In the present research the attempt was made to study the influence of increased pressure upon these phenomena.

The combustions of sulphur was performed in dry oxygen and in iron vessels, for those of nitrogen a drilled piece of cast steel was used, which formed an "autoclave" of 28 c. c. capacity, lined inside with platinum. The inflammation was performed with the aid of a platinum wire, of 0.15 to 0.2 m. m. thickness, which by means of the electric current was momentarily heated to its melting point. For this purpose two insulated pieces of thick platinum wire had been introduced through the head of the autoclave. These acted at the same time as a support for pieces of sulphur or carbon. The air was compressed by a powerful air pump. Oxygen and detonating gas were condensed by the pressure formed by developing these gases in a closed space. Oxygen was developed from a mixture of equal parts of  $\text{KClO}_3$  and  $\text{MnO}_2$  in a retort formed from a bent iron tube of thick wall. A small iron digester served for the preparation of detonating gas in which water, acidulated by  $\text{H}_2\text{SO}_4$ , was decomposed electrolytically. The digester itself was the cathode, while a piece of platinum sheet, well insulated, led into it. During the performance of the experiments the apparatus was surrounded by a protective screen formed of boxes filled with sand. When very high pressures were used the experiments were performed with the aid of mirrors, so that operations were possible without endangering the experimenter.

This mode of arranging the experiments has the advantage that no combustion takes place during the time of compression ; combustion occurs at comparatively low pressures when using a pump. Thus oxygen will set on fire the leather packing at about 40 atm. It is evident that even when using asbestos packing (which Wroblewsky used in his experiments on condensation of gases), the combustion of detonating gas cannot be avoided. The compression of the gases sets free so much heat, that the temperature of combustion is reached at a pressure of several hundred atmospheres. Lead disks which were used for packing will resist a pressure of several thousand atmospheres. The pressures were read by means of manometers furnished by Schaeffer and Budenberg.

The experiments with sulphur show that it is possible to convert half of the amount used directly into sulphuric anhydride. When the digester was opened fumes appeared as when a bottle of sulphuric anhydride is opened. When water was introduced hissing occurred.

The experiments with a mixture of nitrogen and detonating gas and those with nitrogen and lignite proved that great quantities of nitrogen may be directly united with oxygen under high pressures. (*Ber. d. Chem. Ges.*, **23**, 1455.) L. H. F.

#### **Formation of Nitrous Acid and Ammonia from Free Nitrogen. O. LOEW.**

Dried platinum sponge, which will not yield to water even traces of either nitrous acid or ammonia, at once furnishes these two bodies when treated with sodium hydrate solution. If

this solution is very dilute (about  $\frac{1}{1000}$ ), nitrous acid reactions are obtained and not those of ammonia. As Nessler's reagent indi-

cates  $\frac{1}{10000000}$  of ammonia just as distinctly as the reaction of Griess' does the same amount of nitrous acid, the conclusion is drawn that two processes take place under the simultaneous influence of the sponge and of the sodium hydrate :

1. Nitrogen, condensed in small quantities together with oxy-

gen upon the platinum sponge, is directly oxidized to nitric oxide, and this then further into nitrous acid.

2. Using concentrated sodium hydrate, the nitrogen also *reacts with water*, forming ammonium nitrite. (*Ber. d. Chem. Ges.*, **23**, 1443.) L. H. F.

**Action of the Electric Arc Light upon Gaseous Bodies and its Use for Demonstrations.** B. LEPSIUS.

The arc light is used with success in quite a number of experiments instead of the induction spark or the dark discharge. The volumetric relations between  $\text{CO}_2$  and CO, of O to CO, of O to  $\text{CO}$  and  $\text{CO}_2$  have so far been studied. (*Ber. d. Chem. Ges.*, **23**, 1418.) L. H. F.

**The Chemical Constitution of Talc.** F. W. CLARKE and E. A. SCHNEIDER.

The stability of talc towards hydrochloric acid is shown, as well as its decomposition on heating, setting free silicic acid.

These facts can only be reconciled with a formula indicating a meta-silicate. (*Ber. d. Chem. Ges.*, **23**, 1537.) L. H. F.

**The Constitution of Solutions.** FR. RÜDORFF.

It follows from this research on the freezing points of solutions of mixed salts, that salts which are able to form double salts react upon each other when dissolved together, even far from the point of saturation. This is not the case for salts that do not form double salts. (*Ber. d. Chem. Ges.*, **23**, 1846.) L. H. F.

**The Carbohydrates of the Sweet Potatoe (*Batatas edulis*).** W. E. STONE.

This research shows that the sweet potatoe does not contain reducing sugar, but cane sugar in quantities of  $1\frac{1}{2}$  to 2 per cent. Baking transforms a considerable amount of the starch into a soluble form, at the same time hydrolizing saccharose to glucose. (*Ber. d. Chem. Ges.*, **23**, 1406.) L. H. F.



**A new Crystallizable Carbohydrate.** A. VON PLANTA and E. SCHULZE.

The nodose roots of *Stachys tubrifera* furnish a crystallizable carbohydrate of the composition  $C_{18}H_{32}O_{16}$ , or a multiple of the same. The body crystallizes with  $3H_2O$ . It has received the name stachyose and belongs to the group which Tollens calls crystallizable polysaccharides, embracing: raffinose (melitose), gentianose and lactosin. The stachyose resembles most this last mentioned one. (*Ber. d. Chem. Ges.*, **23**, 1692.) L. H. F.

**On a Second Monobrombenzol.** F. FITTICA.

A. Hand has not only disputed the existence of the author's fourth monobromphenol,\* but also that of his second monobrombenzol. In rebuttal, Fittica describes the precautions to be taken in the preparation of this second monobrombenzol which boils at  $62^{\circ}C$ ., while the common monobrombenzol has the boiling point  $155^{\circ}C$ . (*Ber. d. Chem. Ges.*, **23**, 1398.) L. H. F.

**A New Method for the Determination of Free and Combined Carbon in Iron or Steel.** OTTO PETTERSSON and A. SMITT.

0.4 to 0.8 grms. of the material, best in the form of filings or as a single thin sheet, is fused with potassium bisulphate. The operation takes from 5 to 12 minutes, or longer when filings are used. The iron is transformed into ferrous sulphate while equivalent quantities of  $SO_2$  are developed. The combined carbon is oxidized to  $CO_2$ , the graphite remains in the shape of bright, crystalline leaves. By means of a current of air, free from  $CO_2$ , sulphur dioxide and carbon dioxide are expelled and absorbed by a measured quantity of caustic soda and baryta lye; thus barium sulphite and barium carbonate are precipitated. The former is oxidized to sulphate by permanganate in slight excess. The liquid is then acidulated with  $HNO_3$  and the  $CO_2$  determined, using aluminium wire to assist in the development of gas.† The

\* New York Acad. Ann., **3**, 67, (1884).

† See Otto Pettersson's method for the determination of  $CO_2$ , page 354.

graphitic carbon is retained in the fused mass which is perfectly white and easily soluble in warm HCl. The graphite is collected on a little platinum filter with asbestos, dried, gently heated and weighed. Then the filter, while glowing, is subjected for a few minutes to a current of air charged with nitrous vapors. After thus burning the graphite, the filter is weighed again and is at once ready for new use. The development of this mode of analysis occupied over three years until the desirable exactness of 0.01 to 0.02 pr. ct. was assured. (*Ber. d. Chem. Ges.*, **23**, 1401.)

L. H. F.

**Experiments for Quantitative Determination of Arsenic by Marsh's Test. Behavior of Arsine towards Potassium Hydrate.** B. KÜHN and O. SAEGER.

The experiments described tend to show that larger quantities of arsenious acid (0.11 grms.  $\text{As}_2\text{O}_3$  dissolved in 25 c. c. water to which a few drops of KOH sol. were mixed), hence, if the latter be added in greater concentration to the hydrogen apparatus, the arsenic is transformed within three hours almost quantitatively into  $\text{AsH}_3$  and from this into elementary arsenic.

Attention is drawn to the fact that an error has crept from Dragendorff's<sup>1</sup> "Lehrbuch" into all others. It is said in Dragendorff that arsine is not decomposed by potassium hydrate, while stibine is entirely decomposed by the same. This is not correct. Arsine is decomposed more slowly and not as perfectly, but the introduction of a potassium hydrate tube in medico-legal cases is not permissible. If antimony should be present it must be separated previously and by precipitation. (*Ber. d. Chem. Ges.*, **23**, 1798.)

L. H. F.

**Determination of Nitric Acid, according to Schulze-Tiemann.** L. SPIEGEL.

Several years ago, when reporting upon the determination of nitric acid in potable water, the author criticised Schulze-Tiemann's method, claiming that it yielded results with an error

<sup>1</sup>Dragendorff, Die gerichtlich-chemische Ermittlung der Gifte. 2 Auflage, S. 633.

of at least 3 per cent. This determination being performed with the aid of ferrous chloride, and conc. HCl, in a partial vacuum, the error referred to may be avoided by using a current of carbon dioxide, free from air, towards the end of the process. Tiemann in a new edition of his "Water analysis," does not accept this modification of the process. The author maintains the value of his proposal; he works from the beginning in a current of CO<sub>2</sub>, and describes a simple apparatus which serves for this determination. (*Ber. d. Chem. Ges.*, 23, 1361.) L. H. F.

**Method for the Determination of Carbon Dioxide. OTTO PETTERSSON.**

A general mode of determining CO<sub>2</sub> quantitatively in all solid and liquid substances. The method is particularly useful for estimating CO<sub>2</sub> in a state of solution or of partial combination *e. g.*, in natural well or sea water. For details of this method see the original article which describes the apparatus used and gives a diagram. A peculiarity of this determination is that a small piece of iron or aluminium wire is used as a hydrogen developer in the vacuum apparatus in which carbon dioxide is set free. This simultaneous generation of minute quantities of hydrogen is claimed as essential, partly in order to drive out all of the CO<sub>2</sub>, partly to prevent bumping. The gases developed are measured while moist in a burette over mercury. Afterwards the CO<sub>2</sub> is absorbed in the ordinary manner by KOH solution in an Orsat tube.

This apparatus has lately been of great service in the analyses of sea water in hydrographic researches in the Skagerack and Kattegatt. The CO<sub>2</sub> was thus determined in more than 110 samples taken from different depths. Franz Müller, in Bonn, makes the apparatus in a most careful manner. (*Ber. d. Chem. Ges.*, 23, 1402.) L. H. F.

## Abstracts of American Patents Relating to Chemistry.

(From the U. S. Patent Office Gazette.)

(Issued July 15th, 1890.)

**432,058.**—Vegetable black. E. A. de Lisle.

Contains as its essential characteristic material the calcined residuum of cinchona bark, from which the genuine has been primarily extracted.

**432,060.**—Composition for preserving eggs. Silas C. Matteson.

Consists of a mixture of ground silica, alumina, peat, ash and clay.

**432,091.**—Phosphatic fertilizer. J. D. Simmons.

Consists of wood ashes, phosphate of lime, muriate of potash, pulverized sulphur, and nitrate of soda.

**432,118.**—Wood filler. B. J. Couhig.

Consists of molasses, water, starch, pulverized gypsum, glue and alcohol.

**432,151.**—Transparent water color paint. R. T. Swenning.

Consists of an aniline dye, water, gum arabic, gelatin, white sugar and alcohol.

**432,190.**—Apparatus for making vinegar. E. E. Murphy, and W. Berkel.

**432,198.**—Process of purifying crude alcohol. G. Guignard.

The process of separating the aldehydes or like products from alcohols in general, and the alcohols of the distillery in particular, through the formation of sulphite compounds of the aldehydes or like products by treating the crude or impure alcohol with alkaline bisulphite or alkaline sulphite and bisulphite to form said sulphite compounds, and separating such compounds and the alcohol from each other.

**432,240.**—Paint compound. A. A. Jackson.

A water and fire proof paint, consisting of coal tar, asphaltum varnish, cane syrup, spirits of turpentine, red mineral, yellow ocher, whiting, water, soda, salt, and alcohol.

**432,251.**—Refining cocoanut oil. A. Smith.

Cocoanut oil is deodorized by boiling with a sulphide, washing, boiling again with a bisulphite and washing.

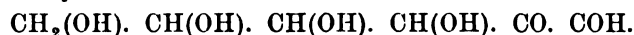
**432,270.**—Carburetor. G. Hargreaves, E. W. Porter, and J. P. Scranton.

**432,280.**—Metallurgical furnace. R. F. Nenninger.

**432,281.**—Apparatus for producing highly heated gas. R. F. Nenninger.



tions for a successful operation. To finely powdered glucosazone the tenfold quantity of fuming HCl is added. It turns dark red, and a portion goes into solution with the same tint. It is thus transformed into its hydrochloride, which, however, is decomposed by water. If the mixture is rapidly heated to 40° C. and vigorously shaken a clear solution is obtained. This is kept for but one minute at 40° C. and then cooled down to 25° C. Now an ample crystallization of phenylhydrazine hydrochloride sets in which indicates the splitting of the osazone. At the same time the dark red tint of the liquid turns to a dark brown. In ten minutes the reaction is finished. The filtered liquid is freed from HCl and the glucosone is precipitated as an insoluble lead compound. It has not, so far, been made to crystallize, and, consequently, could not be analyzed, but its reactions, which correspond absolutely to those of glyoxal and with 1, 2-diketones, do not leave any doubt, that the compound is the aldehyde of fruit sugar and possesses the formula :



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In studying the sugars the osazones are capable of application to other purposes.

The formulæ  $C_6H_{12}O_6$ ;  $C_6H_{10}O_5$ ;  $C_7H_{14}O_7$ , etc., showing the same percentage composition, the analysis alone of these sugars will never allow to decide in regard to the number of carbon atoms; we are therefore forced to analyze a derivative. For this purpose the osazones are best fitted since, as a rule, they may be obtained in a very pure state. They have been utilized so far for the determination of the empirical formulæ of arabinose<sup>20</sup>, sorbine<sup>21</sup> and xylose<sup>22</sup>.

In still other cases the osazones offer a new means of determining the constitution of a sugar. In former times rhamnose (isodulcite) was considered to be a hexatomic alcohol and an analogue of mannite, although its reducing action upon alkaline copper sol. was known. But the use of the hydrazin test showed, in furnishing<sup>23</sup> an osazone,  $C_6H_{10}O_3(N_2H.C_6H_5)_2$ , that the anhydrous rhamnose is a sugar of the formula  $C_6H_{12}O_5$ , for which later on the structural formula was found<sup>24</sup> to be  $CH_3.CH(OH).CH(OH).CH(OH).CH(OH).COH$ .

Another example is offered by milk sugar, which, as we know, is an anhydride of equal molecules of glucose and galactose. Its faculty of forming an osazone proves that it still contains one group— $CH(OH).COH$ . Since, furthermore, the osone which is formed from the osazone decomposes into galactose and glucosone when boiled with dilute acids, it follows that we find in sugar of milk the unchanged aldehydic group of the glucose molecule.<sup>25</sup>

This conclusion, which has been corroborated by the preparation of lactobionic acid<sup>26</sup> and by the hydrolysis of this latter, has led to a new conception of the constitution of milk sugar and of the closely related maltose.

Finally the hydrazones and osazones proved to be particularly valuable for the discovery of new sugars and of substances similar to sugars. These latter are obtained in a comparatively easy manner by moderate oxidation by polyatomic alcohols. As far as I know, it was Carlet<sup>27</sup> who made the first observation of this kind.

<sup>20</sup> Kiliari, *Ber. d. Chem. Ges.*, **20**, 345.

<sup>21</sup> E. Fischer, *Ber. d. Chem. Ges.*, **20**, 827.

<sup>22</sup> Tollens und Wheeler, *Ann. Chem. (Liebig)*, **254**, 315.

<sup>23</sup> Fischer und Tafel, *Ber. d. Chem. Ges.*, **20**, 1091.

<sup>24</sup> Fischer und Tafel, *Ber. d. Chem. Ges.*, **21**, 2173; see also Maquenne, *Compt. Rend.*, **109**, 603.

<sup>25</sup> Fischer, *Ber. d. Chem. Ges.*, **21**, 2633.

<sup>26</sup> Fischer und Meyer, *Ber. d. Chem. Ges.*, **22**, 361.

<sup>27</sup> *Jahresbericht für Chemie* (1860), 250.

(To be continued.)

## ABSTRACTS.

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### GENERAL CHEMISTRY.

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#### Combustion under High Pressure. W. HEMPEL.

It is a known fact, that the combustion of sulphur furnishes noticeable quantities of sulphuric anhydride along with sulphur dioxide. Also that hydrogen, illuminating gas or carbon when burned, allows the formation of nitrous acid easily to be shown. In the present research the attempt was made to study the influence of increased pressure upon these phenomena.

The combustions of sulphur was performed in dry oxygen and in iron vessels, for those of nitrogen a drilled piece of cast steel was used, which formed an "autoclave" of 28 c. c. capacity, lined inside with platinum. The inflammation was performed with the aid of a platinum wire, of 0.15 to 0.2 m. m. thickness, which by means of the electric current was momentarily heated to its melting point. For this purpose two insulated pieces of thick platinum wire had been introduced through the head of the autoclave. These acted at the same time as a support for pieces of sulphur or carbon. The air was compressed by a powerful air pump. Oxygen and detonating gas were condensed by the pressure formed by developing these gases in a closed space. Oxygen was developed from a mixture of equal parts of  $\text{KClO}_3$  and  $\text{MnO}_2$  in a retort formed from a bent iron tube of thick wall. A small iron digester served for the preparation of detonating gas in which water, acidulated by  $\text{H}_2\text{SO}_4$ , was decomposed electrolytically. The digester itself was the cathode, while a piece of platinum sheet, well insulated, led into it. During the performance of the experiments the apparatus was surrounded by a protective screen formed of boxes filled with sand. When very high pressures were used the experiments were performed with the aid of mirrors, so that operations were possible without endangering the experimenter.



This mode of arranging the experiments has the advantage that no combustion takes place during the time of compression ; combustion occurs at comparatively low pressures when using a pump. Thus-oxygen will set on fire the leather packing at about 40 atm. It is evident that even when using asbestos packing (which Wroblewsky used in his experiments on condensation of gases), the combustion of detonating gas cannot be avoided. The compression of the gases sets free so much heat, that the temperature of combustion is reached at a pressure of several hundred atmospheres. Lead disks which were used for packing will resist a pressure of several thousand atmospheres. The pressures were read by means of manometers furnished by Schaeffer and Budenberg.

The experiments with sulphur show that it is possible to convert half of the amount used directly into sulphuric anhydride. When the digester was opened fumes appeared as when a bottle of sulphuric anhydride is opened. When water was introduced hissing occurred.

The experiments with a mixture of nitrogen and detonating gas and those with nitrogen and lignite proved that great quantities of nitrogen may be directly united with oxygen under high pressures. (*Ber. d. Chem. Ges.*, **23**, 1455.) L. II. F.

#### **Formation of Nitrous Acid and Ammonia from Free Nitrogen. O. LOEW.**

Dried platinum sponge, which will not yield to water even traces of either nitrous acid or ammonia, at once furnishes these two bodies when treated with sodium hydrate solution. If this solution is very dilute (about  $\frac{1}{1000}$ ), nitrous acid reactions are obtained and not those of ammonia. As Nessler's reagent indicates  $\frac{1}{10000000}$  of ammonia just as distinctly as the reaction of Griess' does the same amount of nitrous acid, the conclusion is drawn that two processes take place under the simultaneous influence of the sponge and of the sodium hydrate :

1. Nitrogen, condensed in small quantities together with oxy-

gen upon the platinum sponge, is directly oxidized to nitric oxide, and this then further into nitrous acid.

2. Using concentrated sodium hydrate, the nitrogen also *reacts with water*, forming ammonium nitrite. (*Ber. d. Chem. Ges.*, **23**, 1443.) L. H. F.

**Action of the Electric Arc Light upon Gaseous Bodies and its Use for Demonstrations.** B. LEPSIUS.

The arc light is used with success in quite a number of experiments instead of the induction spark or the dark discharge. The volumetric relations between  $\text{CO}_2$  and CO, of O to CO, of O to CO and  $\text{CO}_2$  have so far been studied. (*Ber. d. Chem. Ges.*, **23**, 1418.) L. H. F.

**The Chemical Constitution of Talc.** F. W. CLARKE and E. A. SCHNEIDER.

The stability of talc towards hydrochloric acid is shown, as well as its decomposition on heating, setting free silicic acid.

These facts can only be reconciled with a formula indicating a meta-silicate. (*Ber. d. Chem. Ges.*, **23**, 1537.) L. H. F.

**The Constitution of Solutions.** FR. RÜDORFF.

It follows from this research on the freezing points of solutions of mixed salts, that salts which are able to form double salts react upon each other when dissolved together, even far from the point of saturation. This is not the case for salts that do not form double salts. (*Ber. d. Chem. Ges.*, **23**, 1846.) L. H. F.

**The Carbohydrates of the Sweet Potatoe (*Batatas edulis*).** W. E. STONE.

This research shows that the sweet potatoe does not contain reducing sugar, but cane sugar in quantities of  $1\frac{1}{2}$  to 2 per cent. Baking transforms a considerable amount of the starch into a soluble form, at the same time hydrolizing saccharose to glucose. (*Ber. d. Chem. Ges.*, **23**, 1406.) L. H. F.

**A new Crystallizable Carbohydrate.** A. VON PLANTA and E. SCHULZE.

The nodose roots of *Stachys tuberifera* furnish a crystallizable carbohydrate of the composition  $C_{18}H_{32}O_{16}$ , or a multiple of the same. The body crystallizes with 3  $H_2O$ . It has received the name stachyose and belongs to the group which Tollens calls crystallizable polysaccharides, embracing: raffinose (melitose), gentianose and lactosin. The stachyose resembles most this last mentioned one. (*Ber. d. Chem. Ges.*, 23, 1692.) L. H. F.

**On a Second Monobrombenzol.** F. FITTICA.

A. Hand has not only disputed the existence of the author's fourth monobromphenol,\* but also that of his second monobrombenzol. In rebuttal, Fittica describes the precautions to be taken in the preparation of this second monobrombenzol which boils at  $62^{\circ}C$ ., while the common monobrombenzol has the boiling point  $155^{\circ}C$ . (*Ber. d. Chem. Ges.*, 23, 1398.) L. H. F.

**A New Method for the Determination of Free and Combined Carbon in Iron or Steel.** OTTO PETTERSSON and A. SMITT.

0.4 to 0.8 grms. of the material, best in the form of filings or as a single thin sheet, is fused with potassium bisulphate. The operation takes from 5 to 12 minutes, or longer when filings are used. The iron is transformed into ferrous sulphate while equivalent quantities of  $SO_2$  are developed. The combined carbon is oxidized to  $CO_2$ , the graphite remains in the shape of bright, crystalline leaves. By means of a current of air, free from  $CO_2$ , sulphur dioxide and carbon dioxide are expelled and absorbed by a measured quantity of caustic soda and baryta lye; thus barium sulphite and barium carbonate are precipitated. The former is oxidized to sulphate by permanganate in slight excess. The liquid is then acidulated with  $HNO_3$  and the  $CO_2$  determined, using aluminium wire to assist in the development of gas.† The

\* New York Acad. Ann., 3, 67, (1884).

† See Otto Pettersson's method for the determination of  $CO_2$ , page 354.

graphitic carbon is retained in the fused mass which is perfectly white and easily soluble in warm HCl. The graphite is collected on a little platinum filter with asbestos, dried, gently heated and weighed. Then the filter, while glowing, is subjected for a few minutes to a current of air charged with nitrous vapors. After thus burning the graphite, the filter is weighed again and is at once ready for new use. The development of this mode of analysis occupied over three years until the desirable exactness of 0.01 to 0.02 pr. ct. was assured. (*Ber. d. Chem. Ges.*, 23, 1401.)

L. H. F.

**Experiments for Quantitative Determination of Arsenic by Marsh's Test. Behavior of Arsine towards Potassium Hydrate. B. KÜHN and O. SAEGER.**

The experiments described tend to show that larger quantities of arsenious acid (0.11 grms.  $\text{As}_2\text{O}_3$  dissolved in 25 c. c. water to which a few drops of KOH sol. were mixed), hence, if the latter be added in greater concentration to the hydrogen apparatus, the arsenic is transformed within three hours almost quantitatively into  $\text{AsH}_3$  and from this into elementary arsenic.

Attention is drawn to the fact that an error has crept from Dragendorff's<sup>1</sup> "Lehrbuch" into all others. It is said in Dragendorff that arsine is not decomposed by potassium hydrate, while stibine is entirely decomposed by the same. This is not correct. Arsine is decomposed more slowly and not as perfectly, but the introduction of a potassium hydrate tube in medico-legal cases is not permissible. If antimony should be present it must be separated previously and by precipitation. (*Ber. d. Chem. Ges.*, 23, 1798.)

L. H. F.

**Determination of Nitric Acid, according to Schulze-Tiemann. L. SPIEGEL.**

Several years ago, when reporting upon the determination of nitric acid in potable water, the author criticised Schulze-Tiemann's method, claiming that it yielded results with an error

<sup>1</sup>Dragendorff, Die gerichtlich-chemische Ermittlung der Gifte. 2 Auflage, S. 633.

of at least 3 per cent. This determination being performed with the aid of ferrous chloride, and conc. HCl, in a partial vacuum, the error referred to may be avoided by using a current of carbon dioxide, free from air, towards the end of the process. Tiemann in a new edition of his "Water analysis," does not accept this modification of the process. The author maintains the value of his proposal; he works from the beginning in a current of  $\text{CO}_2$ , and describes a simple apparatus which serves for this determination. (*Ber. d. Chem. Ges.*, **23**, 1361.) L. H. F.

**Method for the Determination of Carbon Dioxide. OTTO PETTERSSON.**

A general mode of determining  $\text{CO}_2$  quantitatively in all solid and liquid substances. The method is particularly useful for estimating  $\text{CO}_2$  in a state of solution or of partial combination *e. g.*, in natural well or sea water. For details of this method see the original article which describes the apparatus used and gives a diagram. A peculiarity of this determination is that a small piece of iron or aluminium wire is used as a hydrogen developer in the vacuum apparatus in which carbon dioxide is set free. This simultaneous generation of minute quantities of hydrogen is claimed as essential, partly in order to drive out all of the  $\text{CO}_2$ , partly to prevent bumping. The gases developed are measured while moist in a burette over mercury. Afterwards the  $\text{CO}_2$  is absorbed in the ordinary manner by KOH solution in an Orsat tube.

This apparatus has lately been of great service in the analyses of sea water in hydrographic researches in the Skagerack and Kattegatt. The  $\text{CO}_2$  was thus determined in more than 110 samples taken from different depths. Franz Müller, in Bonn, makes the apparatus in a most careful manner. (*Ber. d. Chem. Ges.*, **23**, 1402.) L. H. F.

## Abstracts of American Patents Relating to Chemistry.

(From the U. S. Patent Office Gazette.)

(Issued July 15th, 1890.)

**432,058.**—Vegetable black. E. A. de Lisle.

Contains as its essential characteristic material the calcined residuum of cinchona bark, from which the genuine has been primarily extracted.

**432,060.**—Composition for preserving eggs. Silas C. Matteson.

Consists of a mixture of ground silica, alumina, peat, ash and clay.

**432,091.**—Phosphatic fertilizer. J. D. Simmons.

Consists of wood ashes, phosphate of lime, muriate of potash, pulverized sulphur, and nitrate of soda.

**432,118.**—Wood filler. B. J. Couhig.

Consists of molasses, water, starch, pulverized gypsum, glue and alcohol.

**432,151.**—Transparent water color paint. R. T. Swenning.

Consists of an aniline dye, water, gum arabic, gelatin, white sugar and alcohol.

**432,190.**—Apparatus for making vinegar. E. E. Murphy, and W. Berkel.

**432,198.**—Process of purifying crude alcohol. G. Guignard.

The process of separating the aldehydes or like products from alcohols in general, and the alcohols of the distillery in particular, through the formation of sulphite compounds of the aldehydes or like products by treating the crude or impure alcohol with alkaline bisulphite or alkaline sulphite and bisulphite to form said sulphite compounds, and separating such compounds and the alcohol from each other.

**432,240.**—Paint compound. A. A. Jackson.

A water and fire proof paint, consisting of coal tar, asphaltum varnish, cane syrup, spirits of turpentine, red mineral, yellow ocher, whiting, water, soda, salt, and alcohol.

**432,251.**—Refining cocoanut oil. A. Smith.

Cocoanut oil is deodorized by boiling with a sulphide, washing, boiling again with a bisulphite and washing.

**432,270.**—Carburetor. G. Hargreaves, E. W. Porter, and J. P. Scranton.

**432,280.**—Metallurgical furnace. R. F. Nenninger.

**432,281.**—Apparatus for producing highly heated gas. R. F. Nenninger.

**482,313.**—Lubricant. R. Hutchison.

Composed of lime combined with margaric, stearic or oleic acid, or any suitable mixture of such acids and mineral or hydrocarbon oil, there being an excess of the acid sufficient to make the mineral or hydrocarbon oil combine with the lime compound.

**482,386.**—Explosive compound. S. D. Smoliauino.

Consists of nitroglycerin, an alcohol, and an absorbent.

**482,388.**—Process of reducing iron ore. C. J. Eames.

**482,487.**—Detergent. P. K. Post, Jr.

Consists of borax, saturated with ammonia, in the form of a paste or semi-solid.

**482,497.**—Welding compound. H. B. Straut and C. B. Shute.

Consists of borax, prussiate of potash ammonium chloride, water and chalk.

*Issued July 22d, 1890.*

**482,540.**—Filter. T. A. Myers.

**482,604.**—Apparatus for producing bisulphites. C. Cornwell.

**482,692.**—Apparatus for producing bisulphite solutions. T. P. Burgess.

**482,698.**—Process of manufacturing alloys of metal of the aluminium group. G. A. Taurie.

The process consists in exposing an intimate mixture of the oxide of the group metal, carbon, and sulphuric acid to an intense heat, mixing therewith filings of the alloying metal, and exposing the mixture to a white heat.

**482,718.**—Apparatus for producing gaseous fuel. J. M. Ayer.

**482,777.**—Fire extinguishing compound. R. T. Van Valkenburg.

Consists of sulphuric acid, a sulphite and a carbonate.

**482,784.**—Manufacture of white lead. J. A. Boand.

The process consists in constantly stirring and agitating a mass of lead oxide in a closed vessel, passing a stream of carbon dioxide into the mass, and simultaneously passing steam laden with vapor of acetic acid into the mass.

**482,808.**—Process of extracting oil from fish. P. C. Vogellus.

**482,815.**—Process of obtaining oxygen from air. A. Brin.

Barium oxide is heated, admitting air thereto until peroxidation takes place, then shutting off the air supply and deoxidizing the barium by reducing the pressure without changing the temperature of the heating chamber.

**482,853.**—Leather blacking. J. J. Baulch, F. C. Steele, W. J. Lees, and J. F. Evans.

A waterproof leather dressing, consisting of beeswax, neat's foot oil, drop black, heel ball and molasses.

**482,861.**—Process of fermenting. E. Carez.

The development of injurious and destructive ferments in the manufacture of syrups, sugar or alcohol, is prevented by subjecting the wort of amylaceous substances to the action of hydrofluoric acid.

**432,926.**—Process of making acetic acid. I. A. T. Bang and M. C. A. Ruffin.

A hot solution of calcium acetate is decomposed with hot sulphuric acid.

**432,939.**—Apparatus for manufacturing wood gas. J. Hanlon.

*(Issued July 29th, 1890.)*

**432,989.**—Blue dye. C. Duisberg.

Produced by the action of the tetrazo compound of benzidinesulphone-disulpho acid upon phenylbetanaphthylamine. In the dry state it is an indigo blue, amorphous powder, difficultly soluble in cold water, easily soluble in hot water and alcohol, insoluble in benzol. In concentrated sulphuric acid it dissolves with red violet color. It dyes unmordanted cotton in alkaline bath, and wool and silk in a neutral bath with a fine indigo blue shade.

**433,066.**—Process of making soap. J. B. N. Berry.

Pine needles are treated with an alkaline solution to extract the resin, after which the fatty materials are added to the solution and saponified.

**433,074.**—Art of silvering mirrors. A. B. Drautz.

A solution for silvering mirrors consisting of ammoniacal silver nitrate, sodium and potassium tartrate, milk sugar, silver sulphate, a lead salt, sulphuric acid and water.

**433,086.**—Process of deoxidizing copper. W. W. Keys.

Copper and its alloys are deoxidized and purified by melting the metal by exposure to the hot products of combustion developed by burning hydrocarbon oils, then raising the molten metal to a high temperature, and then while practically excluding atmospheric oxygen further exposing the metal to the flaming products of combustion afforded by the oil.

**433,119.**—Process of making potash soap. H. Eurich.

A strong solution of caustic potash is added to a fat, and the mixture kept at a high heat until a product is obtained, which on cooling is a hard potash soap.

**433,126.**—Gas purifier. J. Hearne.

**433,129.**—Process of manufacturing and in the composition of refractory cements. W. S. Lea.

The process consists of the following steps : Disintegrating materials whose chemical composition is chiefly that of a compound silicate of alumina and of alkalies and earthy bases, mixed with quartz by subjecting the same to the simultaneous action of heat and vapors of nitric and hydrochloric acids, reducing the disintegrated materials and mixing there-with silicious materials whose composition is chiefly hydrated silicate of



alumina, together with calcium phosphate and carbonate, caustic potash and manganese, again reducing the compound and mixing therewith sodium chloride and an alkaline silicate. •

**433,181.**—Process of ageing wine. G. H. Malter.

Consists in passing the wine through vapors produced by heating another wine.

**433,185.**—Apparatus for decomposing metallic salts. O. B. Peck.

**433,152.**—Extracting fats and oils. M. Schroeder.

The materials containing fats and oils are subjected to the elutriating action of sulphurous acid, after which the sulphurous acid is removed by distillation and condensation.

**433,185.**—Dental vulcanizer. J. E. Quinn.

**433,215.**—Insulating compound. I. Rabinowicz.

Consists of tartaric acid, a tartrate, gilsonite and palm stearin pitch.

**433,326.**—Process of preparing wood pulp. W. N. Cornell.

**433,336.**—Apparatus for oxygenating and carbureting air. C. Fiesse.

**433,341.**—Regenerative gas lamp. E. Tullford.

**433,395.**—Obtaining pepsin. J. Brill.

The process consists in, first, finely chopping hogs' stomachs; second, subjecting the prepared mass to the action of acid and water, and heating it for about three hours; third, pressing the juice from the mass; fourth, clarifying the juice by a benzine bath, and then drying the precipitated pepsin.

*(Issued August 5th, 1890.)*

**433,455.**—Solidified perfume. G. H. Dubelle.

Consists of paraffin intimately mixed with powdered orris root and a volatile perfume.

**433,495.**—Carburetor. A. B. Smith.

**433,534.**—Apparatus for washing the fumes of sulphur. T. W. Montgomery and J. Warnke.

**433,537.**—Glass tube cutter. T. McGar.

**433,603.**—Regenerative furnace. S. R. Smythe.

**433,604.**—Regenerative furnace. S. R. Smythe.

**433,658.**—Lump fuel of coal, charcoal or coke screenings. A. Mayer.

A lump or block fuel, composed of coal, coke or charcoal screenings or dust, a glutinous substance, an oleaginous substance, a plastic substance, and a fibrous substance combined with silicate of soda.

**433,729.**—Process of manufacturing butter. G. H. Hamrick.

The raising of cream from milk is effected by the action of sulphurous acid gas.

**433,784.**—Process and apparatus for manufacturing, heating and illuminating gas. C. F. Hadley.

The process consists in burning fluid hydrocarbon in conjunction with

air and steam, then condensing and eliminating the aqueous vapor from the gaseous product, and then reheating the product in conjunction with fluid hydrocarbon.

**433,790.**—Process of dyeing. T. Ingham.

A process of dyeing woven or knitted fabrics of mixed animal and vegetable fibres (such as yarns woven together in the gray state), consisting in first submitting the mixed fabric to a bath of the required coloring matter or solution without any mordant; second, dyeing the fabric; third, oxidizing the coloring material on the dried fabric by passing the same through a solution having the property of fixing the colors both upon the vegetable and animal fibres at one and the same time.

**433,802.**—Apparatus for the manufacture of gas. K. M. Mitchell.

**433,861.**—Composition of matter for plaster. De L. Haigh.

A compound for admixture with lime, etc., in the formation of plaster, consisting of fine silicious material coated with a soluble sulphate and borax.

**433,877.**—Disinfectant. W. F. Simes.

Consists of naphthalene, oil of camphor, and caustic soda.

**433,890.**—Process of purifying water. P. Degener.

Organic impurities are precipitated by adding magnesium carbonate, then lime or its equivalent is added to precipitate the magnesia, and finally, a chemical, such as carbon dioxide is added, to precipitate the excess of the precipitant.

**433,898.**—Insulating material. J. Tottrell.

Consists of a mixture of india rubber and aluminium.

**433,899.**—Artificial plaster. H. Leichsenring.

Consists of glycolline, plaster of paris, water and coloring matter.

**433,926.**—Apparatus for the manufacture of gas. J. B. Archer.

*(Issued August 12th, 1890.)*

**434,016.**—Antifriction compound. H. B. Devlan.

Consists of bamboo fiber, paper pulp, asbestos, plumbago, and a sizing, such as sodium silicate.

**434,039.**—Explosive compound. H. S. Maxim.

The process of manufacturing consists in mixing and agitating pyroxyline or gun cotton with a compound of nitroglycerin, castor oil, and a proportion of a solvent, such as acetone, insufficient to dissolve the entire gun cotton, then subjecting the product in a partial vacuum to the action of acetone, and then to pressure.

**434,074.**—Process of sugar refining. L. Sternberg.

An improvement in the art of refining low grade sugars, molasses, syrups, or vegetable juices, consisting, first, in boiling the saccharine solution with a suitable quantity of lime, or its equivalent, thereby decomposing the glucose present, and then separating the resulting insoluble

glucose compounds by filtration ; and, secondly, in treating the remaining solution with acid, and precipitating and removing by a second filtration the resulting lime compounds and the remaining impurities present, preparatory to subjecting the solution thus freed from glucose and injurious compounds resulting from the decomposing of the glucose to further treatment for the extraction of the crystallizable sugar.

**484,184.**—Furnace for melting glass. L. Houze.

**484,248.**—Combined fertilizer and insecticide. L. J. Carlile and G. B. Rumph.

Consists of refuse tobacco, bran, cotton seed meal, paris green, powdered hellebore, arsenious oxide and India berries.

**484,287.**—Process of manufacturing nitrocellulose. G. M. Mowbray.

**484,288.**—Machine for the continuous manufacture of nitrocellulose. G. M. Mowbray.

**484,296.**—Flux or solution for coating metals. B. S. Richardson.

A solution for the preparation of iron for coating it with lead, consisting of zinc chloride, oxalic acid, ammonium chloride, and sodium sulphite.

**484,330.**—Varnish. W. D. Field.

Consists of saturated solutions of pyroxyline and resins or gum resins in suitable solvents.

*Issued August 19th, 1890.*

**484,490.**—Composition of matter for mortar. M. Furley, G. W. Chamberlin and P. M. Pomeroy.

Consists of ashes, sand, marble dust, plaster of paris, shorts, and sugar or other saccharine matter.

**484,493.**—Blue dye. A. Weinberg.

Has the chemical constitution of a disulphonated tertiary dibenzyl derivative of thionine, and shows the following characteristics: it is easily soluble in water with a bright blue color, less soluble in alcohol, insoluble in ether; it dissolves in strong sulphuric acid with a green color, which is changed into blue by addition of water; by reducing agents it is transformed into leucosulpho acid. It dyes animal fibre in an acid bath a greenish blue.

**484,502.**—Muffle furnace for desulphurizing ores. G. H. Chick.

**484,556.**—Fireproof paint. J. T. Durkee.

Consists of gas tar, asbestos and clay.

**484,569.**—Plastering composition. W. Robinson.

Consists of sawdust saturated with a solution of quicklime, alum, and white lead with plaster of paris, glue and sand.

**484,570.**—Filter. W. H. Sargent.

**484,471.**—Filter. W. H. Sargent.

**484,621.**—Apparatus for the manufacture of gas. J. B. Archer.

**484,623.**—Process of making white lead. A. C. Bradley.

Consists in subjecting a solution of the basic acetate of lead containing between 10 and 12 per cent. of the basic acetate in a slowly moving thin sheet to the joint action of heat of about 120° F and carbon dioxide.

**434,645.**—Process of treating hides. J. Schmitt.

The process consists in coating the fleshy side of the hides with a warm solution of fresh slaked lime and water while the hair is on the hides, and then piling them one upon the other with the hairy side down and allowing them to remain in this condition from half an hour to an hour, this step in the process serving to raise the hides and increase the thickness thereof, and preceding the usual steps of the depilating lime bath.

**434,666.**—Water purifying apparatus. O. H. Jewell and W. M. Jewell.

**434,694.**—Process of reducing iron ores with heated gases. C. Adams.

**434,696.**—Process of extracting oil. C. F. Binder.

Consists in subjecting the material from which the oil is to be extracted to direct contact with superheated or dry steam of such a high temperature that only sufficient moisture is applied to the material to take the place of the oil in the cells, and then expressing the oil.

**434,739.**—Method of manufacturing articles for containing petroleum. H. Thame.

Vessels, pipes and other receptacles are made by saturating or impregnating a bibulous paper with a solution of shellac, and then wrapping it layer upon layer to the thickness required, the layers being united by interposed films of shellac.

**434,790.**—Stove polish. S. A. Kingsland.

Consists of water, borax, shellac, wax and burned cork.

**434,798.**—Paint. J. G. W. Mastens.

Consists of water, bone black, charcoal, red lead, boiled linseed oil and saltpetre.

**434,831.**—Filter press. F. Kleemann.

*(Issued August 26th, 1890.)*

**434,941.**—Gas washer. W. Morava.

**434,948.**—Mixer for natural gas. A. A. Phillips.

**434,977.**—Process of preparing fertilizers. C. Clifford.

Refuse leather is dampened and placed in heaps to sweat or ferment, after which the heaps are opened and exposed to the air. These operations are repeated as long as the fermentation continues, and the resulting product is ground or passed through sieves.

**435,000.**—Apparatus for cooling and aerating wort for malt liquors. C. D. Stanford.

**435,009.**—Apparatus for burning hydrocarbon oils. J. H. Bullard and F. A. Nickerson.

**435,050.**—Composition of manganese and iron for brake shoes. W. W. Snow.

An alloy containing 5 to 15 per cent. manganese.

**485,070.**—Apparatus for the manufacture of illuminating gas. P. W. Mackenzie.

**485,071.**—Process of manufacturing illuminating gas. P. W. Mackenzie.

The process consists in evaporating hydrocarbon oil, mixing the products of evaporation with the products of combustion of hydrocarbon oil, steam and oxygen or air, conveying away the gaseous products resulting therefrom and fixing them, employing the fixed gas to evaporate the hydrocarbon oil and conveying away the heavy unevaporated oil and residual products at different levels below the oil being evaporated.

**485,076.**—Artificial fuel. A. Pagenstecher.

Consists of pulverized coal, charcoal or coke, and starch, saltpetre, and brown sandstone.

**485,096.**—Funnel. H. W. Hoops.

The bell of the funnel is provided with undercut ribs.

**485,129.**—Process of crystalizing soda alum. E. Augé.

A solution of aluminium and sodium sulphates is concentrated to a specific gravity of between 1.32 and 1.42 and cooled until it assumes a pasty consistency. The paste is then exposed in layers, upon inclined surfaces, to a temperature between 15 and 20° C. till the mother liquors are separated, whereby crystals of uniform composition and size are obtained.

**485,198.**—Process of refining crude asphaltum. R. Alexander.

The process consists in dessicating crude asphaltum, recovering the condensable oil given off during the desiccation, and subsequently returning said oils to the desiccated material.

**485,269.**—Apparatus for burning hydrocarbons. J. H. Bullard.

**485,270.**—Hydrocarbon burning apparatus. J. H. Bullard.

**485,280.**—Process of making ammonium nitrate. E. Carey.

Barium sulphate is calcined out of contact with air with a mixture of charcoal and resin oil (or other hydrocarbon), and the product of the reaction boiled with sulphur and water to produce a polysulphide. This is then converted into barium nitrate by means of sodium nitrate. The crystalized barium nitrate is finally decomposed with ammonium sulphate.

*(Issued September 2d, 1890.)*

**485,421.**—Battery compound. E. M. G. Hewett.

Consists of chromic oxide and ammonium chloride dissolved in water and combined with sulphuric acid or its equivalent.

**485,464.**—Ammonia still. G. Stroh and G. Osius.

**485,485.**—Composition of matter for artificial stone. J. Elliott.

Consists of Kentish rag, Portland or York stone, finely sifted Bath stone dust and water mixed with Portland cement.

**485,509.**—Insecticide. W. Mann.

Consists of flowers of smart weed, lime and sulphur.

**435,670.**—Regenerative gas burner. F. Stellwag.

**435,720.**—Apparatus for the manufacture of gas. J. B. Archer.

**435,747.**—Diffusion apparatus. L. F. Hauptman.

**435,760.**—Apparatus for galvanizing. C. E. Matteson.

**435,784.**—Apparatus for the treatment of cane juice. J. J. Adams and L. W. Tracy.

**435,856.**—Carburetor. L. C. Parker.

**435,862.**—Process of making carbon tetrachloride. E. G. Scott.

The process consists in passing dry chlorine gas slowly through carbon bisulphide and iodine, separating the carbon bisulphide and carbon tetrachloride, which is formed from the sulphur chloride by distillation, then fractioning the tetrachloride and treating it with caustic alkali to remove the iodine. The concentrated aqueous solution of iodine is treated with a strong mineral acid and chlorine to set free the iodine. This is extracted with carbon bisulphide and the solution is used in the first step of the process.

**435,911.**—Preserving compound. O. Williams.

Consists of ground coffee berries, ground cinchona bark and ground cinnamon mixed with flowers of sulphur, pulverized sugar and pulverized potassium nitrate.

*(Issued September 9th, 1890.)*

**435,922.**—Process of tanning hides. T. L. Crafton.

The process consists in first immersing the hides in a mixture consisting of fifteen gallons of water, six quarts slaked lime, six quarts ashes and one pound of soda; second, removing the lime from the hides by immersing them in a bath consisting of twenty gallons salt water, one peck of wheat bran, two gallons of buttermilk, half pound of acetic acid (6%) or strong vinegar, and three pounds of salt; third, submerging then in a tan ooze consisting of fifteen gallons of water, ten pounds of gambier, four pounds of salt, three pounds of saltpetre and one pound of acetic acid (6%) or strong vinegar.

**435,940.**—Compound for converting wrought iron into steel. W. J. Miles, Jr.

Consists of potassium ferrocyanide, glycerrhizinum ammoniatum, and ammoniacum.

**436,029.**—Apparatus for charging inclined gas retorts. L. VanVestrandt.

**436,044.**—Filtering apparatus. R. E. Miller.

**436,133.**—Process of separating fats from emulsions. C. D. Hellström.

The emulsions are subjected simultaneously to centrifugal force and to temporary accelerations parallel or nearly so with the axis on which the centrifugal force is generated.

- 436,199.**—Percolator. W. D. Warwick and C. E. Cunningham.  
**436,225.**—Insulator. J. C. Firth.  
Consists of pumice stone.  
**436,227.**—Apparatus for extracting oils with the acid of solvents. W. T. Forbes.  
**436,244.**—Method of and apparatus for the production of mineral wool. W. H. Kennedy.  
**436,250.**—Substitute for iodoform. J. Messinger and G. Vortmann.  
A red brown odorless powder derived from iodine and salicylic acid, which is insoluble in water, alcohol, ether, and oil, changing to a bright red powder by heating it with mineral acids and melting at about 225° C., with decomposition, and being insoluble in alkalis.

*(Issued September 16th, 1890.)*

- 436,414.**—Tower for condensing acid. C. Graham.  
**436,497.**—Steel alloy. R. Hadfield.  
Contains chromium, together with manganese and silicon.  
**436,534.**—Process of manufacturing beer. A. J. Metzler.  
Consists in maintaining the beer under a partial vacuum during the ruh stage until it has ripened, then adding a small proportion of saccharine matter, and permitting the carbonic acid gas developed to relieve the vacuum in the cask and beer.  
**436,535.**—Process of making beer. A. J. Metzler.  
**436,536.**—Process of manufacturing beer. A. J. Metzler.  
**436,587.**—Process of preparing ruh beer for market. A. J. Metzler.  
**436,587.**—Process of producing photographic films. J. Schwartz.  
The sensitiveness to light is increased by treating the film with formaldehyde.  
**436,599.**—Composition for making fabrics fireproof. R. R. Graf.  
Consists of ammonium sulphate, ammonium phosphate, ammonium chloride, lime, sodium tungstate, and water.  
**436,623.**—Apparatus for making extracts. G. S. Andres.  
**436,624.**—Apparatus for making extracts. G. S. Andres.  
**436,633.**—Process of purifying brines. M. M. Monsanto.  
Uses trisodium phosphate.  
**436,684.**—Apparatus for and process of continuous rectification of spirits, alcohol, etc. E. A. Barbet.  
**436,733.**—Insulating material. J. W. Easton.  
Consists of soapstone, waterproofing material and a fibrous substance.  
**436,735.**—Process of and apparatus for manufacturing alcohol. G. Gingnard and A. Hédouin.  
**436,764.**—Process of and apparatus for rectifying and distilling alcohol. E. A. Barbet.

*(Issued September 23d, 1890.)*

**436,812.**—Apparatus for making hydrogen gas. J. W. Tallmadge.

**436,881.**—Apparatus for the manufacture of oil gas. D. E. Teal.

**436,882.**—Apparatus for making coke and gas. C. N. Trump.

**436,895.**—Process of electro-depositing aluminium. J. A. Jeançon.

Consists in subjecting a supersaturated solution of an oxysalt of aluminium in water to the action of an electrolytic current passed through the electrolyte between an anode plate of aluminium in a state of division or porosity, and a suitable metallic cathode to be plated.

**436,898.**—Manufacture of explosives. H. S. Maxim.

Consists in confining gun cotton in a receiver, exhausting the air from the same, then introducing a vaporized solvent into the exhausted receiver until the gun cotton is partially dissolved, then compressing it, and then dividing it up into small pieces or grains.

**436,975.**—Gas generator. C. W. Gibson.

**436,994.**—Standpipe for ammonia gas generators. M. Poschinger and H. Vogt.

**437,098.**—Gas producer. J. W. Culmer.

**437,136.**—Gas machine. J. S. Wood.

**437,140.**—Process of calcining gypsum. J. Sickler.

**437,163.**—Process of manufacturing artificial fuel. W. B. McClure.

**437,164.**—Artificial fuel. W. B. McClure.

Consists of pulverized culm or coal dust, sand, calcined lime dust, and solid and naturally liquid asphaltums.

W. R.





REGULAR MEETING, OCTOBER 3, 1890.

Vice-President Breneman in the chair: The minutes of the previous meeting were read and accepted. The following gentlemen were unanimously elected to membership:

Stephen H. Emmens, Emmensite Explosive Co., Emmens, Pa.

F. E. Thompson, Headmaster Rogers High School, Newport, R. I.

Dr. Geo. Archbold, Chemist U. S. Navy, Washington, D. C.

G. C. Caldwell, Ph.D., Professor of Agricultural Chemistry, Cornell University, Ithaca, N. Y.

Chas. E. Colby, Ph.D., Professor of Organic Chemistry, School of Mines, N. Y.

W. H. Seaman, Professor of Analytical Chemistry, Missouri School of Mines, Rolla, Mo.

Chas. E. Pellew, Assistant in Chemistry, School of Mines, N. Y.

Hugh Hamilton, M.D., Harrisburg, Pa.

Edward Gudeman, Honorary Assistant in Chemistry, School of Mines, N. Y.

Dr. Alfred Springer, President Springer Torsion Balance Co., 46-50 E. 2d street, Cincinnati, O.

Dr. H. J. Wheeler, Chemist Agricultural Experiment Station, Kingston, R. I.

Dr. Edward S. Wood, Professor of Chemistry, Harvard Medical School, Cambridge, Mass.

Dr. S. A. Lattimore, Professor of Chemistry, University of Rochester, Rochester, N. Y.

Chas. E. Brewer, Professor of Chemistry, Wake Forest University, Wake Forest, N. C.

R. W. Jones, Professor of Chemistry, University of Mississippi, Oxford, Miss.

Peter T. Austen, Professor of Chemistry, Rutgers College, New Brunswick, N. J.

Harry Snyder, Instructor in Chemistry, Cornell University, Ithaca, N. Y.

Dr. Chas. G. Curtman, 3718 N. 9th street, St. Louis, Mo.

B. B. Goldsmith, Ph.B., Chemist American Lead Pencil Co., 19 E. 74th street.

F. A. Owen, S.B., Chemist Burlington Woolen Co., Burlington, Vt.

The nominee for associate membership, S. V. V. Huntington, Manager Edw. Smith & Co., 158 William street, N. Y., was unanimously elected.

The following were proposed as members :

James E. Talmadge, D.S.D., Ph.D., Principal Latter Day Saints College, Salt Lake City, Utah.

J. A. Burns, Ph.D., Vice-Pres. and General Manager Tallapoosa Furnace Co., Tallapoosa, Ga.

S. G. Valentine, Colebrook Furnace, Lebanon, Pa.

H. F. Carpenter, Assayer, etc., 29 Page street, Providence, R. I.

W. C. Ferguson, Ph.B., Chemist Laurel Hill Chemical Works, 138 Wilson street, Brooklyn, N. Y.

Walter M. Saunders, Hughesdale, R. I.

Dr. J. H. Washburn, Kingston, R. I.

Harry Mullikin, Newport, R. I.

Dr. Edward P. Haws, Dept. of Chemistry, Amherst College, Amherst, Mass.

H. S. Patterson, 121 Pleasant street, Worcester, Mass.

The paper of E. F. Ladd on "Investigation upon Maize" was read by title.

Dr. Friedburg read a second portion of his "Studies on Resins."

In the order of miscellaneous business it was moved that a General Meeting be held in Philadelphia during the holidays, and that a committee be appointed to make arrangements for this meeting. Carried.

Messrs. Rupp, Woodman and Sabin were appointed a nominating committee, to present names of officers to be balloted for at the annual meeting in December.

The meeting was then adjourned.

CHAS. F. McKENNA,

Recording Secretary.

## INVESTIGATION UPON MAIZE.\*

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BY E. F. LADD.

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In the Spring of 1888 the writer planned and began a series of investigations upon maize, for the purpose of gaining information upon several mooted questions, particularly the following :

1. What chemical changes take place in maize as it approaches maturity?
2. In what stage of maturity is it most advisable to cut maize for ensilage?
3. What chemical changes take place in, and what loss results from the process of converting maize into ensilage?
4. What is the loss and what the nature of the chemical changes that take place in maize during the process of field and barn curing?
5. What is the digestibility of, and what the relative nutritive value of the above several products?

These experiments and investigations, begun in 1888, were continued into the Winter of 1889-90, when it became necessary to abandon all efforts at legitimate scientific research, and, while many data were secured the work of research can hardly be said to have reached any satisfactory state of completion—in fact, it is hardly begun as originally outlined. That the writer will not have an opportunity to carry the investigation further, seems a

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\*The data for a part of the first of this article will be many found in the eighth annual report of the New York Agricultural Experiment Station. Some of the data relating to the digestibility of ensilage and field cured maize may be found in a paper, "Ensilage and Dry Fodder," presented to the Society for the Promotion of Agricultural Science at the Indianapolis meeting, August, 1890. The whole is here brought together in order that it may be made more accessible, and much data heretofore unpublished included.

justifiable reason for presenting these fragmentary notes to serve as landmarks to those who may be engaged in similar lines of research.

The first year little more was accomplished than to inaugurate the work and to go carefully over the ground to see what was needed; besides, the maize grown, a Southern variety (Burrill and Whitman) could not possibly mature in Central New York, and this proved an obstacle to our work. The field under experiment contained a little less than two acres; one-half was cut September 11, the remainder September 29. At the first date the maize varied from silking to watery stage of kernel, and the last from watery to milky stage. The yield per acre was as follows:

	Sept. 11. Lbs.	Sept. 29. Lbs.
Total maize per acre.....	25,326	25,011
Water.....	20,322	19,351
Dry matter.....	5,004	5,660
Ash.....	215	237
Albuminoids.....	525	512
Crude fibre.....	1,443	1,650
Nitrogen-free extract.....	2,696	3,109
Fat (ether extract).....	125	188

On further investigation we find the changes that have taken place to be mainly in the albuminoids and nitrogen-free extract, and the extent of these changes is shown by the following:

	Sept. 11. Lbs.	Sept. 29. Lbs.
Total nitrogen.....	84	81
Albuminoid nitrogen.....	50	67
Amide nitrogen.....	34	14
Invert sugar.....	580	751
Sucrose.....	390	634
Starch.....	908	1,077

We first note that there was no increase in total nitrogen—even an apparent loss—but that much of the nitrogen in the form of amides was transformed into albuminoids, and this trans-

formation and translocation our experiments have invariably seemed to show to be accompanied by a loss of nitrogen, and it would seem natural that this should be so. While there was an increase of 413 pounds in nitrogen-free extract between the two periods of harvesting, the sugars and starches included in the nitrogen-free extract increased 583 pounds, showing that much which was in a transitory state had been built up to higher and more organized products—sugar and starch.

## INVESTIGATIONS IN 1889.

Without further considering these results we pass to the investigation made the second year. This season, 1889, a flint variety of maize (King Philip) that would in any favorable season mature a good stand of ears, was selected for the main experiment, although the same variety as grown the previous year was under trial. In a field of about twelve acres, one acre, representative of the whole field was selected for experimental work. This acre was divided into five equal lots to be cut at different times, representing various stages of growth and to serve as a basis for our calculations and chemical examinations. From each cutting eight samples were taken for analyses, so we have as fair an average as seemed possible to secure from a product so difficult to sample. The dates of cutting and stage of growth were as follows :

Date of Cutting.	Stage of Growth.
July 30 .....	Full tasseled.
August 9 .....	Full silked.
August 21 .....	Kernels watery to full milk.
September 7 .....	Kernels glazing.
September 23 .....	Ripe.

The yield of maize per acre and the per cent. of water in same were as follows :

	Pounds Per Acre.	Per Cent. Water.
July 30 .....	18,045	91.05
August 9 .....	25,745	88.05
August 21 .....	32,000	85.766
September 7 .....	32,295	77.70
September 23 .....	28,460	72.18

## DRY MATTER HARVESTED PER ACRE.

From the data already given we may calculate the amount of dry matter actually harvested at the several stages of growth :

	Maize, tons Per Acre.	Tons Water Per Acre.	Tons Dry Matter Per Acre.
July 30.....	9.02	8.21	.81
August 9.....	12.87	11.33	1.54
August 21.....	16.30	13.97	2.33
September 7.....	16.14	12.51	3.63
September 23....	14.23	10.27	3.96

The above table is suggestive and confirms what has been repeatedly asserted, that maize so planted as to come only to the tasseling or silking stage of growth, is principally water and furnishes but little nutritive matter to animals forced to eat the forage.

The chemical composition of the maize cut at the several dates in respect to dry substance is given below :

	July 30.	Aug. 9.	Aug. 21.	Sept. 7.	Sept. 23.
Ash.....	8.53	6.54	5.00	4.20	4.60
Albuminoids.....	14.881	14.19	10.31	8.94	8.56
Crude fibre.....	31.76	28.36	27.18	24.38	21.90
Nitrogen-free ex't....	40.39	45.46	52.58	58.87	60.97
Fat.....	4.46	5.45	4.93	3.60	3.97
Total nitrogen.....	2.37	2.27	1.65	1.43	1.37
Alb. nitrogen.....	1.69	1.45	1.30	1.09	1.15
Amide nitrogen.....	.68	.82	.35	.34	.23
Invert sugar.....	3.60	9.76	14.32	10.00	6.80
Sucrose.....	.56	3.60	2.80	1.32	1.88
Starch.....	17.55	15.96	15.20	24.09	36.02

The chemical composition gives but a small idea of the real changes that have taken place; this can only be learned by considering the totals which are given in the following :

	Tasseled July 30. lbs.	Silked Aug. 9. lbs.	Milk Aug. 21. lbs.	Glazed Sept. 7. lbs.	Ripe Sept. 28. lbs.
Yield per acre.....	8,045	25,745	32,600	32,295	28,460
Water per acre.....	16,426	22,666	27,957	25,093	20,542
Dry matter per acre..	1,619	3,078	4,643	7,202	7,918
Ash .....	139	201	232	302	364
Albuminoids .....	240	437	479	644	678
Crude fibre.....	514	873	1,262	1,756	1,734
Nitrogen-free ex't....	654	1,399	2,441	4,240	4,828
Fat.....	72	168	229	260	314
Total nitrogen.....	38	70	77	103	108
Albuminoid nitrogen	27	45	60	78	91
Amide nitrogen.....	11	25	17	24	17
Invert sugar.....	58	300	665	720	538
Sucrose .....	9	111	129	95	149
Starch .....	122	491	707	735	2,853

The last table indicates several interesting features not the least of which is the seeming confirmation of a previous observation. That is that in the growth of the maize plant there are two periods of little or no increase in total nitrogen. The first is during the early formation of the ear, between the period of silking and watery stage of kernels; the other between the periods of glazing and full maturity. In fact, while I have not the necessary data to show it, yet I feel confident from observations made that there is at these times not only no material increase in the nitrogenous constituents, but that there is an actual loss of nitrogen incident to the transformation and translocation going on at this time in the plant. This would suggest the possibility of an advantage to be derived by making application of easily soluble nitrogenous fertilizers at two distinct periods in the life of the maize plant. We may also note the marked increase of starch during the latter stage of the maturation. As maize is preeminently a carbonaceous plant and as starch its most valuable constituent to be preserved, we can see the importance of allowing the plant to come as near to full maturity as is possible, and at the same time of allowing it to be utilized for



the purpose designed. Observation has shown that if maize is to be grown for ensilage, maturation may proceed too far, so far that if the plant be stored in the silo it will mould, decay, and become almost or even quite worthless for feeding. It is important that we possess more definite knowledge on this particular point, and our investigation was continued with that end in view.

#### MAIZE FOR THE SILO.

For furthering our work, two silos of about eleven tons' capacity each were available. Of each silo three sides were of cement and one of wood. Incidentally we may remark that the ensilage was much better preserved on those sides where the contact was with wood than on those with cement.

One of the silos was filled with the dent variety of maize (B. and W. corn) at about the milky stage of the kernel, September 5. This maize, after it was carefully weighed, was sampled for analyses as it was passed through an ensilage cutter that cut the stalk into one and one-fourth inch pieces. Twenty-seven samples were taken for water determination, and these were united into four lots, representing various depths in the silo, and complete analyses made for each lot.

The second silo was filled September 13, with the flint variety of maize, between the stage of glazing and full maturity, as indicated in a previous table, showing the composition of the maize cut at the various stages of growth. We now have two silos filled with maize at two stages of growth; it would be better were they of the same variety, but we will continue the comparison under the conditions as they exist.

#### ENSILAGE FROM IMMATURE MAIZE.

The silo filled with immature maize September 5 was opened on October 10, the top or surface having been covered in the meantime with tarred paper and lightly weighted about the corners of the silo.

The results of the analyses of the maize as put into the silo and of the ensilage as taken out is shown in the next table.

A represents the ensilage from the bottom of the pit and E that from the surface.

## ANALYSES OF IMMATURE MAIZE FOR ENSILAGE.

		Water.	Dry Matter.	Ash.	Albuminoids.	Crude Fibre.	Nitrogen-Free Extract.	Fat.
Maize	A. ....	81.18	18.82	4.53	9.94	28.12	53.83	3.58
"	B. ....	80.39	19.61	4.50	10.06	25.83	56.14	3.47
"	C. ....	81.48	18.52	4.75	9.25	28.16	54.92	2.92
"	D. ....	81.81	18.19	5.07	11.18	26.37	53.43	3.75
Average .....		81.08	18.92	4.71	10.11	27.12	54.38	3.68

## \*ANALYSES OF ENSILAGE FROM IMMATURE MAIZE.

Ensilage	A. ....	83.37	16.63	5.84	9.37	32.32	44.71	7.76
"	B. ....	82.98	17.02	4.32	9.06	32.17	50.13	4.32
"	C. ....	82.18	17.82	6.02	9.25	31.58	48.88	4.47
"	D. ....	84.11	15.89	5.98	9.12	33.36	45.73	5.81
"	E. ....	84.86	15.14	7.69	11.12	33.12	44.26	3.81
Average .....		83.50	16.50	5.97	9.58	32.50	46.71	5.23

The sample A contains less water than the average for the silo, yet in removing the last foot of ensilage from the bottom of the pit, there was so much juice that it would ooze quite rapidly through the open spaces in the box used for weighing up the ensilage. The low per cent. of water in the ensilage, from the bottom of the silo was something of a surprise, but it seems, from our own and other experiments, that there was probably a diffusion of soluble matter from above into the lower part of the silo, so that this liquid probably contained in solution or suspension considerable solid matter. During the 36 days that the maize remained in the silo there was a loss in total weight of 5.13 per cent., and of dry matter, as calculated from the water determination, of 13.50 per cent. It should be borne in mind that these silos

\*Since our investigation had to do only with the practical side of the question, no account was taken of the nitrogen that existed in the ensilage as ammonia, for as such it would be valueless to the agriculturist.

were of small capacity, 10 to 12 tons only, so that we should expect the loss in pr. ct. to be greater than for a large silo of 100 to 150 tons capacity. The following table gives the actual results as found for the maize as put into the silo, and the ensilage as taken out :

	Put in Silo, lbs.	Taken out of Silo, lbs.	Loss or Gain per cent.
Total weight.....	23,382	22,291	5.13—
Total water.....	18,958	18,466	—
Total dry matter.....	4,424	3,825	13.50—
Ash.....	208	207	.69—
Albuminoids.....	447	349	21.99—
Crude fibre.....	1,199	1,310	9.24+
Nitrogen-free extract.....	2,406	1,777	26.13—
Fat.....	163	182	11.83+
Total nitrogen.....	22	55	23.75—
Albuminoid nitrogen.....	49	35	28.55—
Amide nitrogen.....	23	20	13.04—
Invert sugar.....	493	88	82.12—
Sucrose.....	373	19	94.77—
Starch.....	625	783	25.22—
Silage per cubic foot.....	—	37.7	—

In the contents of this silo the loss was mainly upon the albuminoids and nitrogen-free extract. The sugars were nearly all destroyed by fermentation, only about 100 pounds remaining against about 800 put into the silo.

#### ENSILAGE FROM MAIZE NEARLY MATURE.

The maize as put in the second silo was cut at period of full glazing, or between the period of glazing and ripeness. It was run through an ensilage cutter and 24 samples were taken for water determination, which samples were united into four lots for analyses representing different depths in the silo. The silo was filled September 13 and opened December 2, the maize being carefully weighed when put in, and when opened the ensilage was taken out in blocks according as the product seemed uniform in general appearance, the same as with the first silo. Of ensilage there were taken 44 samples, of about 2 kilos each, for water determination,

and these were united into five lots representing the several depths in the silo. Again, A indicates the sample from the bottom and E that from the top of the silo.

## ANALYSES OF MATURE MAIZE FOR ENSILAGE.

	Water.	Dry Matter.	Ash.	Albuminoids.	Crude Fibre.	Nitrogen-free extract.	Fat.
Maize A .....	76.28	23.52	3.38	10.25	21.30	60.94	4.13
" B .....	72.41	27.59	2.90	9.06	21.09	62.02	4.93
" C .....	74.47	25.53	3.19	10.12	22.58	59.97	4.14
" D .....	75.82	24.18	3.48	9.56	22.91	59.13	4.92
<b>Average .....</b>	<b>74.93</b>	<b>25.07</b>	<b>3.24</b>	<b>9.77</b>	<b>21.97</b>	<b>60.49</b>	<b>4.53</b>

## ANALYSES OF ENSILAGE FROM MATURE MAIZE.

Ensilage A .....	80.34	19.66	6.39	7.75	26.18	55.22	4.46
" B .....	77.67	22.33	4.31	7.63	27.67	55.57	4.82
" C .....	76.92	23.08	4.30	8.56	24.04	58.00	4.90
" D .....	79.10	20.90	4.70	8.44	26.38	56.79	3.69
" E .....	75.22	24.78	6.39	9.87	26.27	54.38	3.09
<b>Average .....</b>	<b>77.85</b>	<b>22.15</b>	<b>5.26</b>	<b>8.45</b>	<b>26.11</b>	<b>55.99</b>	<b>4.19</b>

The ensilage came out in exceedingly good condition, and the average of several determinations gave but 0.28 per cent. of acid calculated as acetic, so that this may be classed among what is commonly termed sweet ensilage; that is, relatively sweet compared with the acid ensilage not unfrequently met with. In total weight there was a loss of 3.25 per cent. during the process, a period of 38 days. Of dry matter there was a loss of 15.21 per cent. These figures must not be interpreted too closely, for although the work from beginning to end was done with all the care I could personally give, yet it is evident that the samples, although 44 were taken from the silo and 24 from the maize as put in the silo, do not fairly represent the true composition of the ensilage as judged by the total ash put in and taken out of the silo. This same fact is true for every investigation thus far made, so far as the results have come under my observation. It would seem then that calculations base

on the ash as a constant to work from, may lead us very far from a true understanding of the actual changes which have taken place in the silo.

I had hoped to make some chemical examinations of the juices and soluble portions from another silo, but was unable to do so. I assume, however, that it will be found that much of the matter contained in the juices at the bottom of the silo is made up of soluble matter diffused from the overlying layers, and the more water contained in the ensilage the greater should we expect to find the diffusion. If this be true, it is plain to see how we may be misled, when but one or two samples are taken from a silo, as to the real conditions that exist. I offer these suggestions hoping that others who are engaged in similar work may find it worthy of further investigation.

Generally it has been supposed that the greatest loss came upon the carbohydrates, but in this case our investigation shows a greater loss per cent. for the albuminoids than for the carbohydrates as a whole. Of the carbohydrates the sugars have suffered the heaviest loss—more than three-fourths of the total amount having disappeared, as will be manifest by the accompanying table:

	Put in silo, lbs.	Taken out of silo, lbs.	Loss or gain per cent.
Total weight.....	21,054	20,368	3.25—
Total water.....	15,776	15,893	
Total dry matter.....	5,278	4,475	15.21—
Ash.....	171	215	25.60+
Albuminoids.....	516	373	27.53—
Crude fibre.....	1,159	1,149	.92—
Nitrogen-free ex't.....	3,193	2,536	20.55—
Fat.....	239	201	15.83—
Total nitrogen.....	82	60	27.53—
Albuminoid nitrogen.....	70	44	37.17—
Amide nitrogen.....	12	16	33.33+
Invert sugar.....	307	65	78.73—
Sucrose.....	190	40	79.24—
Starch.....	1,938	1,437	25.98—
Per cent. acid in ensilage.....		0.28%	
Ensilage to the cubic foot.....		35 lbs.	

An inspection of the preceding table shows the sugars to have been largely lost by chemical changes which took place in the ensilage and the albuminoids to the extent of more than one-fourth of the total amount. No investigation was made to determine the kind and nature of the fermentation that took place, but to the careful observer it seemed evident that the changes were not wholly alike for the two silos, and, further, that the class of ferments was not the same for all parts of the same silo. Thus near the surface of the ensilage in the silo both observation and the chemical products indicated that a different ferment was at work from that at the middle of the silo or near the bottom, each of which seemed to have characteristic properties peculiar to that part of the silo. Had I been competent to do so I would have made a study of these changes along with a determination of the ultimate chemical products, but this field of research is a broad and difficult one, requiring great skill, so no attempt was made to study the biological side or even to trace the proximate chemical products, as the two fields, for a thorough study of this subject, are inseparable.

I stated that it seemed probable that the kind of fermentation was not the same for all parts of the silo. My reasons for this statement are two. Careful observation of the ensilage as removed from the silo showed unmistakable difference in appearance for those parts of the silo—top, centre and bottom—and these observations led me to note more carefully the chemical composition of the ensilage. The maize as put in the silo was very uniform, but that at the bottom of the silo was shown by analyses to have the largest per cent. of albuminoids; still this difference was not marked. Now, had the changes been similar throughout, then the relation of the albuminoids to the other constituents should have remained about the same, or rather the highest per cent. of albuminoids should have been at the bottom of the silo. The chemical analyses show the reverse of this to be true, while the ensilage near the surface contained over two per cent. more albuminoids than that near the bottom of the silo.

The changes that took place near the surface in the silo seemed to have been more processes of decay and oxidation dependent upon the oxygen of the air for their action while near the bottom,

the albuminoids seemed to have been the active agents in promoting the continued fermentation. Judged by the ash, the greatest loss was near the surface and at the bottom of the silo. Undoubtedly this is true for the surface, but it seems probable that the accumulation of ash near the bottom came as the result of diffusion, as already indicated.

#### MAIZE, FIELD CURED.

At the same time that the second silo was filled, another lot of maize from the same field was selected by taking here and there a bundle, so as to have it represent a fair average of the entire lot. This was put in shocks in the field and there left for curing. The maize was cut September 13, and remained standing in the field until October 21, when it was drawn to the barn, weighed, run through the cutter and sampled for analyses. The following table shows the results of the investigation :

	Calculated Sept. 13, lbs.	Found Oct. 21, lbs.	Loss or Gain per cent.
Total weight.....	2,348	1,055	----
Total water.....	1,759	533	----
Total dry matter.....	589	522	11.25—
Ash.....	19	23	21.05+
Albuminoids.....	56	38	32.06—
Crude fibre.....	129	140	8.52+
Nitrogen-free extract.....	356	294	17.41—
Fat.....	27	16	40.74—
Total nitrogen.....	9.1	6.1	32.89—
Albuminoid nitrogen.....	7.7	4.5	41.54—
Amide nitrogen.....	1.4	1.6	15.00+
Invert sugar.....	34.	22.	35.14—
Sucrose.....	21.	6.	71.43
Starch.....	227.	Undetermined	----

The loss of albuminoids in field curing maize was even greater than for the ensilage, and in a period of 38 days, the loss in dry matter amounted 11.25 per cent. or nearly as great as for one of the silos. The increase in ash was probably due to the earth that

adhered to the butts of the stalks since they stood upon the loose soil. The rain during this period was not excessive, but there was much damp, cloudy weather.

#### MAIZE, BARN CURED.

A second lot of maize, taken in the same manner as that for field curing, was reserved for barn curing. This was drawn to the barn, weighed, and then put in good condition for drying by standing the bundles openly against a fence near the barn. It was hoped this lot might be dried for storing without having any rain fall upon it, but in this we were disappointed, since one quite heavy rain wet it down before it was in condition to go into the barn for storing. The bundles were then put in a barn loft, where they remained until November 13th or just two months from date of harvesting. The results are shown by the following table :

	Calculated Sept. 13, lbs.	Found Nov. 13, lbs.	Loss or Gain per cent.
Total weight.....	2,690	1,034	34.87—
Total water.....	1,916	414	—
Total dry matter.....	774	620	19.98—
Ash.....	25	26	4.74+
Albuminoids.....	76	43	42.66—
Crude fibre.....	170	176	3.64+
Nitrogen-free extract.....	468	357	23.86—
Fat.....	35	17	51.24—

Up to date of closing my connection with the station, I had not found opportunity to complete the further analytical work with this part of the investigation.

These results are somewhat astounding, especially regarding loss of albuminoids; but with the best of care, the Autumn was so damp and cloudy, that the fodder moulded badly in the barn although well spread about in an open space.

These are the results of but single experiments, and need to be repeated again in detail before any positive facts can be ascertained. Yet it would seem from these trials that there is no greater loss of nutritive matter in a silo properly filled with good



maize, than for the same plant, field or barn cured, as is commonly practised.

#### DIGESTION EXPERIMENTS.

Having considered somewhat in detail our investigation with the maize as growing, as dried fodder and as ensilage, we have now to record the result of our experiments for determining the digestibility of its several products. The digestibility of ensilage from immature maize, from the matured and for the field cured maize was determined. For our subject of experimentation we had two heifers, the same animals used in the digestion work the winter previous. The heifer Star was due in calf in February, while Spot was an unbred animal. The animals were put in the experimental feeding barn at the station, October 7, and preceding each trial one week's preliminary feeding was had with the same fodder and in like quantities as during the digestion proper, in order that the digestive tract might become cleared of all traces of other food. Watchmen were stationed with the animals night and day and the dung and urine caught in separate pails, and at once transferred to covered galvanized iron receptacles, sufficiently large to hold the voidings for 24 hours. Each noon the dung and urine were carefully weighed on a Fairbanks silk scale, sensitive to one-fourth ounce and an aliquot part of the well mixed dung taken for water determination. These last samples were then united for further analyses.

#### EXPERIMENT NO. 1.

In this trial ensilage from the immature maize was tested. The chemical composition of the ensilage fed was as follows :

	Per Cent.
Water .....	82.58
Dry matter .....	17.42
	<hr/>
	100.00
DRY SUBSTANCE.	
Ash .....	4.32
Albuminoids .....	9.06
Crude fibre .....	32.17
Nitrogen-free extract .....	50.13
Fat .....	4.32
Albuminoid nitrogen .....	0.87

Amide nitrogen .....	0.58
Total nitrogen .....	1.45
Invert sugar .....	2.08
Sucrose .....	.36
Starch .....	21.20

The weights of the animals for ten consecutive days, the last four being the digestion period proper, are shown below :

	STAR. lbs.	SPOT. lbs.
Oct. 10 .....	1,091	1,114
" 11 .....	1,108	1,100
" 12 .....	1,096	1,086
" 13 .....	1,087	1,088
" 14 .....	1,087	1,080
" 15 .....	1,081	1,078
" 16 .....	1,089	1,074
" 17 .....	1,086	1,076
" 18 .....	1,092	1,078
" 19 .....	1,089	1,076

These figures indicate that ensilage of the kind under experiment hardly served for maintenance when fed as the exclusive feed.

The average temperature of the barn for each two hours, as recorded by a self-registering thermometer, is shown below :

## TEMPERATURE OF BARN.

TIME.	OCTOBER							
	12	13	14	15	16	17	18	19
12:2 A. M. ....	50	49	47	46	51	51	56	54
2:4 " .....	49	48	46	46	51	51	55	53
4:6 " .....	48	47	46	45	51	50	54	53
6:8 " .....	48	47	46	44	50	49	53	52
8:10 " .....	49	47	43	45	51	50	51	51
10:12 " .....	50	46	46	47	52	52	53	52
12:2 P. M. ....	54	47	49	49	55	56	56	56
2:4 " .....	53	47	49	51	57	58	58	57
4:6 " .....	52	47	49	53	58	57	57	58
6:8 " .....	50	46	47	53	55	57	56	57
8:10 " .....	50	46	47	52	52	56	55	55
10:12 " .....	49	46	47	52	51	57	54	55

The amount of ensilage fed per day to each animal was sixty pounds, as expressed in tabular form we have:

	STAR.	SPOT.
Ensilage fed per day .....	960.00 ozs.	960.00 ozs.
Water per day .....	154.00 ozs.	246.00 ozs.
Ensilage eaten per day .....	958.46 ozs.	957.54 ozs.

The animals drank no water during the entire period they were fed on ensilage although water was offered twice each day.

The amount of dung per day and the per cent. of water is shown below :

	STAR.		SPOT.	
	Ozs.	% water.	Ozs.	% water.
Oct. 16 .....	309.5	83.37	398.7	84.07
Oct. 17 .....	387.0	84.88	358.0	85.27
Oct. 18 .....	389.5	84.74	401.5	85.73
Oct. 19 .....	344.7	83.99	368.7	85.00

The urine voided, per day together with per cent. of nitrogen in the urine, is given below :

	STAR.		SPOT.	
	Ozs.	% nitrogen.	Ozs.	% nitrogen.
Oct. 16 .....	398.0	.271	401.5	.250
Oct. 17 .....	344.2	.307	314.7	.359
Oct. 18 .....	342.5	.325	280.7	.381
Oct. 19 .....	322.7	.337	157.2	.390

Analyses of the water-free dung, gave the following results :

	STAR.	SPOT.
Ash .....	11.11	11.57
Albuminoids .....	12.87	12.87
Crude fibre .....	29.32	27.83
Nitrogen-free extract .....	44.60	45.76
Fat .....	2.10	2.06
Albuminoid nitrogen .....	1.80	1.78
Crude nitrogen .....	.26	.28
Total nitrogen .....	2.06	2.06

The data for the digestion coefficients are presented in the next table :

	DRY MATTER.		ALBUMI- NOIDS.		CRUDE FIBRE.		NITROGEN- FREE EXTRACT.		FAT.	
	Star. OZS.	Spot. OZS.	Star. OZS.	Spot. OZS.	Star. OZS.	Spot. OZS.	Star. OZS.	Spot. OZS.	Star. OZS.	Spot. OZS.
Total eaten.....	166.63	166.58	15.41	15.41	53.59	53.59	83.52	83.50	7.19	7.19
Dung.....	56.16	57.22	7.23	7.36	16.47	15.92	25.05	26.18	1.18	1.18
Digested.....	110.47	109.36	8.18	8.05	37.12	37.67	58.47	57.32	6.01	6.01
Per cent. digested.....	66.36	65.65	53.06	52.23	69.26	70.29	70.00	68.67	83.58	83.58
Average.....	66.00		52.65		69.77		69.32		83.58	

## EXPERIMENT No. 2.

In this trial the same animals were used as in the previous one. The fodder was the field cured maize already reported upon. The chemical composition of the maize proved to be as follows :

	Per cent.
Water.....	50.48
Dry matter.....	49.52
Dry substance.....	100.00
Ash.....	4.43
Albuminoids.....	7.31
Crude fibre.....	28.81
Nitrogen-free extract.....	56.34
Fat.....	3.11
Albuminoid nitrogen.....	.87
Crude nitrogen.....	.30
Total nitrogen.....	1.17
Invert sugar.....	4.30
Sucrose.....	1.20
Starch.....	32.37

During the trial, the weights of the animals were as shown below, the last four days being the time for which the dung was saved:

	STAR.	SPOT.
Oct. 22.....	1,099	1,074
Oct. 23.....	1,081	1,062
Oct. 24.....	1,080	1,074
Oct. 25.....	1,082	1,074
Oct. 26.....	1,086	1,086
Oct. 27.....	1,082	1,066
Oct. 28.....	1,099	1,075
Oct. 29.....	1,100	1,079
Oct. 30.....	1,102	1,078
Oct. 31.....	1,095	1,079
Nov. 1.....	1,101	1,088

It will be seen from an inspection of the last table that the animals consumed just about enough for maintenance.

The average temperature of the barn for each two hours as recorded by a self-registering thermometer is shown in tabular form below:

TIME.	OCTOBER.								Nov.
	24	25	26	27	28	29	30	31	1
12- 2 A. M. ....	43	46	50	55	52	50	50	49	54
2- 4 " .....	45	--	50	55	51	50	49	48	53
4- 6 " .....	46	--	50	55	51	50	49	48	53
6- 8 " .....	48	--	50	55	51	50	49	48	53
8-10 " .....	50	--	51	54	51	50	49	48	52
10-12 " .....	50	46	52	54	50	50	49	49	52
12- 2 P. M. ....	49	47	54	55	50	50	50	49	52
2- 4 " .....	49	47	54	55	49	50	50	50	--
4- 6 " .....	48	49	55	54	50	50	50	50	--
6- 8 " .....	49	49	55	54	50	51	50	51	--
8-10 " .....	47	49	55	53	50	50	49	52	--
10-12 " .....	45	49	55	52	50	50	49	52	--

The amount of fodder fed each animal per day was 25 pounds, as in tabular form we express the results, as follows:

	Star. Ozs.	Spot. Ozs.
Fodder fed per day.....	400.0	400.0
Waste per day.....	.4	4.65
Fodder eaten per day.....	399.6	395.35

The amount of water drunk per day was as follows:

	Star. Lbs.	Spot. Lbs.
Oct. 28 .....	17.0	25.0
“ 29 .....	15.5	28.5
“ 30 .....	15.3	29.6
“ 31 .....	16.2	24.6
Nov. 1 .....	4.4	29.2

The amount of dung per day and per cent. of water in same, is here given :

	Star.		Spot.	
	Ozs.	% Water.	Ozs.	% Water.
Oct. 29 .....	341.5	77.63	400.7	81.82
“ 30 .....	356.5	77.94	396.2	81.59
“ 31 .....	337.0	76.84	396.7	81.86
Nov. 1 .....	322.5	76.34	394.2	83.19

The urine voided per day together, with per cent. of nitrogen contained in same, are here given :

	Star.		Spot.	
	Ozs.	% Nitrogen.	Ozs.	% Nitrogen.
Oct. 29 .....	112.0	.585	180.0	.590
“ 30 .....	157.7	.650	121.0	.622
“ 31 .....	102.0	.715	141.5	.671
Nov. 1 .....	143.5	.584	189.5	.522

Analysis of the water from dung gave the following results :

	Star.	Spot.
Ash.....	7.22	8.68
Albuminoids.....	11.81	12.75
Crude fibre.....	22.75	21.46

Nitrogen-free extract.....	56.09	55.05
Fat.....	2.13	2.06
Alb. nitrogen.....	1.69	1.72
Amide nitrogen.....	.20	.32
Total nitrogen.....	1.89	2.04

Having now the essential data we may consider the results of the digestion proper :

	DRY MATTER.		ALBUMINOIDS.		CRUDE FIBRE.		NITROGEN FREE EXTRACT.		FAT.	
	Star. Ozs.	Spot. Ozs.	Star. Ozs.	Spot. Ozs.	Star. Ozs.	Spot. Ozs.	Star. Ozs.	Spot. Ozs.	Star. Ozs.	Spot. Ozs.
Total eaten .....	201.65	198.90	17.74	14.54	58.09	57.90	113.62	112.06	6.27	6.18
Dung.....	77.35	71.01	9.13	9.03	17.59	15.24	43.38	39.09	1.65	1.46
Digested.....	124.30	127.89	5.61	5.49	40.50	42.06	70.24	70.24	4.62	4.72
Per cent. digested...	61.64	64.29	38.05	37.75	69.72	73.40	61.82	65.11	73.68	76.37
Average .....	62.96		37.72		71.56		63.46		75.02	

One point worthy of note is the low coefficient of digestibility for the albuminoids in the above results.

#### EXPERIMENT NO. 3.

The same animals were the subjects in this trial as in the previous ones and the food was the ensilage from mature maize already discussed.

The chemical composition of the ensilage fed was, as follows :

	Per cent.
Water .....	76.92
Dry matter.....	23.08
Dry substance.....	100.00
Ash .....	4.50
Albuminoids .....	8.56
Crude fibre.....	24.04
Nitrogen-free extract.....	58.00
Fat .....	4.90

Albuminoid nitrogen.....	.95
Amide nitrogen.....	.42
Total nitrogen.....	1.37
Invert sugar.....	1.28
Sucrose.....	.92
Starch.....	34.08

The weights of the animals taken each morning before receiving food or water are given below :

	STAR.	SPOT.
Nov. 22.....	1,107	1,084
23.....	1,112	1,083
24.....	1,109	1,085
25.....	1,111	1,078
26.....	1,110	1,081
27.....	1,111	1,080
28.....	1,107	1,084
29.....	1,106	1,086
30.....	1,103	1,076

The average temperature for each two hours at the barn is recorded below :

TIME.	NOVEMBER.									
	21	22	23	24	25	26	27	28	29	30
12- 2 A. M. ....	47	47	46	45	50	39	42	48	45	42
2- 4 " .....	47	47	47	46	50	39	42	49	45	42
4- 6 " .....	45	47	47	45	49	39	41	49	45	42
6- 8 " .....	46	48	47	43	49	39	40	49	45	42
8-10 " .....	47	48	47	42	46	40	40	47	43	42
10-12 P. M. ....	49	49	47	43	45	40	40	46	43	41
12- 2 " .....	50	50	47	46	45	41	41	42	44	41
2- 4 " .....	51	50	47	49	43	42	41	42	42	42
4- 6 " .....	51	50	46	50	44	42	41	43	41	
6- 8 " .....	49	48	45	50	43	43	42	44	42	
8-10 " .....	48	47	45	50	42	43	44	43	42	
10-12 " .....	47	47	45	50	41	43	45	43	42	



The amount of ensilage fed each day was 50 pounds with results as follows :

	STAR. Ozs.	SPOT. Ozs.
Ensilage fed per day .....	800.	800.
Water per day .....	0	0
Ensilage eaten per day .....	800.	800.

Roth animals refused water although offered twice each day.

The amount of dung per day and per cent. of water in same are shown below :

	STAR.		SPOT.	
	Ozs.	% Water.	Ozs.	% Water.
Oct. 27 .....	265.5	80.44	284.0	83.44
" 28 .....	314.7	82.22	356.5	84.25
" 29 .....	334.5	81.23	300.5	84.00
" 30 .....	325.5	81.35	322.5	83.20

The urine voided per day together with the per cent. of nitrogen are indicated below :

	STAR.		SPOT.	
	Ozs.	% Nitrogen.	Ozs.	% Nitrogen.
Oct. 27 .....	209.5	.364	170.0	.600
" 28 .....	227.5	.321	189.0	.550
" 29 .....	279.0	.337	297.2	.464
" 30 .....	281.2	.311	290.5	.400

The chemical composition of the water from dung was as follows :

	STAR.	SPOT.
Ash .....	8.11	9.08
Albuminoid .....	11.75	11.62
Crude fibre .....	23.88	23.63
Nitrogen-free extract .....	54.13	53.41
Fat .....	2.13	2.26

The digestibility of the ensilage as determined from the data given is shown by the following table :

	DRY MATTER.		ALBUMI- NOIDS.		CRUDE FIBER.		NITROGEN FREE EXTRACT.		FAT.	
	Star.	Spot.	Star.	Spot.	Star.	Spot.	Star.	Spot.	Star.	Spot.
Total eaten, ozs.....	184.64	184.64	15.80	15.80	44.39	44.39	107.09	107.09	9.05	9.05
Dung, ozs .....	57.91	53.86	6.80	6.26	13.83	13.73	31.34	28.76	1.23	1.23
Digested, ozs.....	126.73	130.78	9.00	9.54	30.56	30.66	75.75	78.33	7.82	7.83
Per cent. digested..	68.63	70.83	56.96	60.37	68.84	69.07	70.73	73.14	86.41	86.53
Average.....	69.73		58.66		68.95		71.93		86.64	

## GENERAL SUMMARIES.

For comparison let us bring together the average results for the three digestive trials :

## COEFFICIENTS OF DIGESTIBILITY.

	Ensilage Immature Maize.	Ensilage Mature Maize.	Field Cured Maize.
Dry matter.....	66.00	69.73	62.96
Albuminoids.....	52.65	58.66	37.72
Crude fibre.....	69.77	68.95	71.56
Nitrogen-free extract..	69.32	71.93	63.46
Fat.....	83.58	86.46	75.02

These trials give a better showing for ensilage from mature maize than for either of the others, but we should bear in mind, however, that the two ensilages are not from the same variety of maize. The field cured maize and ensilage from mature maize were identical products from the same lot and harvested at the same date.

Carrying our comparison still further, using the data already secured, one ton of the original maize would furnish, of digestible matter, as follows, expressed in pounds :

	Ensilage Immature Maize.	Ensilage Mature Maize.	Field Cured Maize.
Dry matter.....	198.9	295.8	270.2
Albuminoids.....	14.4	21.0	11.9
Crude fibre.....	67.6	76.3	91.7
Nitrogen-free extract..	104.7	170.8	159.1
Fat.....	10.9	15.3	13.8

So far as our investigation has been carried the results are in favor of ensilage from maize well advanced towards maturity, and we feel confident that the ensilage of the future will be from maize that has the corn glazed.

In closing I wish to thank W. H. Whalen, assistant chemist, and R. D. Newton, laboratory attendant, for their incessant fidelity in all the details of this investigation.

New York City, September 15, 1890.

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\*Since this article was read Mr. Ladd has been appointed Prof. of Chemistry in the Dakota Agricultural College, Fargo, N. Dakota, and Director of the Experiment Station.—*Ed.*

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## STUDIES UPON RESINS.\*

BY L. H. FRIEDBURG, PH. D.

### II.

In order to determine exactly the temperature of melting kauri gum and the vapors arising from the same, simultaneously, the following experiment was performed, in which I was assisted by Professor A. H. Sabin, in whose laboratory the work was done.

222 grms. of coarsely powdered kauri (copal) gum, very pale but rather soft, known in the New York market as "four crosses" gum, was put into a retort 125 m.m. in diameter and 125 m.m. deep from the bottom of the bulb of the retort to the lower side of the throat.

Through the tube were inserted two thermometers (mercury un-

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\*See J. Amer. Chem. Soc., 12, 285. and foot note, 287.

der nitrogen), in the following way. One reached 190 mm. below the upper end of the cork, and had its bulb just covered by the gum. The cork covered the space from  $+110^{\circ}$  to  $+130^{\circ}$  C and the  $315^{\circ}$  point was 230 m.m. above the cork. The other reached 95 m.m. below the cork, thus having its bulb in the vapor. The cork covered the graduation from  $+38^{\circ}$  C. to  $+57^{\circ}$  C., the  $180^{\circ}$  C. point being 150 m.m. above the cork. With shorter thermometers the temperatures recorded would have been higher, and in the case of the extreme temperature reached,  $351^{\circ}$  C., would probably have been  $15^{\circ}$  or  $20^{\circ}$  higher if the thermometer could have been immersed in the liquid. The temperatures observed were as follows :

	Vapor.	Gum.
After 5 minutes .....	$115^{\circ}$ C.	—
10    " .....	149 "	—
15    " .....	163 "	$166^{\circ}$ C.
20    " .....	166 "	210 "
25    " .....	152 "	260 "
30    " .....	168 "	269 "
35    " .....	174 "	293 "
40    " .....	173 "	297 "
45    " .....	166 "	327 "
50    " .....	167 "	343 "
55    " .....	181 "	351 "
60    " .....	178 "	341 "
65    " .....	175 "	337 "
70    " .....	175 "	335 "

The burner was removed 23 minutes from the beginning of the operation and replaced 5 minutes later. For the first 18 minutes the retort was filled with visible fumes, which only partly condensed in the attached Liebig's condenser. They then disappeared and the upper half of the retort remained transparent until the close of the operation. The liquid distillate obtained in this case weighed only 36 grms. The residue in the retort was poured hot into a metallic vessel, shallow and wide, and allowed to cool. It was then transparent, clear and of a brilliant, dark amber color. It proved to be completely soluble in cold spirits of turpentine.

The distillate consisted of two layers, the lighter forming about 80 per cent. of the whole and showing a spec. grav. of 0.86 at + 21°C. The heavier liquid had a specific gravity near 1.01 at the same temperature.

*College of the City of New York, October, 1890.*

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### THE INFLUENCE OF TARTRATES AND LACTATES UPON THE DIGESTION OF ALBUMINOIDS.

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BY LUCIUS PITKIN, PH. B.

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In the digestion of albuminoids the chief agent is the gastric juice; upon its composition as regards strength in acid and in the amount of pepsin present depends the rapidity of its action and the completeness of the change it induces in the conversion of albuminoids into peptones.

It is obvious, therefore, that any chemical compound dissolved in the gastric juice which either modifies its acidity or influences by its action the pepsin itself will exert a corresponding effect upon gastric digestion.

Prof. Chittenden of Yale University has published (*Philadelphia Medical News*, February 16, 1889) data concerning the retarding influence of many chemical substances on the peptic digestive process. It may be stated as a general rule with but few exceptions that in experiments with hydrochloric acid pepsin solution the addition of soluble salts exercises an inhibitory action on the conversion of albuminoids into peptones.

Not only is a certain acidity necessary for the best digestive action, but the character of the acid is even more important than the strength. Hydrochloric acid, the natural acid of the gastric juice is, as many experimenters have shown, the most powerful of the acids in its proteolytic action when combined with pepsin. As a generalization from the experiments recorded it may be remarked that the mineral acids have been found to favor diges-

tive action in their combination with pepsin to a larger extent than the milder organic acids. Thus with oxalic acid one and one-half per cent. (1.5%) "dissolves about three-fourths as much proteid as the same amount of pepsin with 0.1 per cent. hydrochloric acid (Chittenden). In reference to acetic acid the same experimenter states "it is practically worthless."

In the course of an investigation made during the present year on the influence of the residues from baking powders upon the digestion of albuminoids some results were obtained which may be of interest and which certainly have a practical bearing on some of the questions which have been raised in the consideration of this class of food products. As is well known the amount of these saline residues is large in using any baking powder but larger in some classes than in others; thus, in proportion to the amount of carbonic acid liberated, the soluble residues of the cream of tartar class largely exceed that of either the alum or phosphate. In the experiments undertaken I have endeavored to obtain some data regarding these residues from cream of tartar powders, alum, and alum and phosphate powders. In addition experiments were undertaken with lactic acid in preference to other organic acids since it is the acid of sour milk and upon its percentage in the milk depends its degree of sourness and the quantity required for neutralizing any given amount of cooking soda. *A priori*, we could reason that the digestive power of gastric juice would be lessened by the residue in bread or biscuit raised with sour milk and soda and the experiment proves this to be a fact.

In some comparisons it has been the practice to compare the action of a certain quantity (*i. e.*, a gramme) of one substance with the same amount of another. This, while of value for some purposes, is also very misleading unless some one versed in the matter both interprets the results and reports them, since, as mentioned before, the residues of the various powders do not always correspond in quantity with their leavening powders. To say then that one gramme of a certain residue inhibits digestion as much as a gramme and a half of a certain other residue may be really to make the better powder appear the worse, since the quantity of

residue to a given weight of bread may vary so widely. I have, therefore, taken the weights of residue produced in neutralizing a like weight of sodium bicarbonate as the proper weights to be compared.

To raise well one quart of flour requires about forty (40) grains of sodium bicarbonate (Cornwall), which is equivalent to  $2\frac{1}{10}$  grammes. I therefore prepared the following solutions :

I.  $2\frac{1}{10}$  grms. sodium bicarbonate and  $5\frac{1}{10}$  grms. cream of tartar in 250 c.c. of water.

II.  $2\frac{1}{10}$  grms. of sodium bicarbonate and enough acetic acid to neutralize it in 250 c.c. of water.

III.  $2\frac{2}{10}$  grms. of sodium sulphate and  $\frac{1}{10}$  grms. ammonium sulphate in 250 c.c. of water.

We thus have in the quarter litre in I. the water-soluble residue when a quart of flour is raised with cream of tartar and soda, in II. when the same quantity is raised with sour milk and soda, and in III. the corresponding amount of soluble residue when burnt ammonia alum is used.

One-fifth (50 c.c.) of each of these was added to the artificial gastric juice.

This was prepared by dissolving 100 milligrammes of pepsin in one litre of  $\frac{1}{10}\%$  hydrochloric acid and in each experiment 50 c.c. were employed. The albumen was coagulated and passed through a 20 mesh sieve to ensure uniformity of sample and an extended surface, and ten grammes of the moist substance were taken in each case.

50 c.c. of hydrochloric acid pepsin solution was poured on 10 grms. of moist albumen; to this was added 50 c.c. of the solution of one of the various residues and the whole digested at 99° F. for  $4\frac{1}{2}$  hours. The digestion was retarded in all cases as is apparent from the following table.

The *undissolved* residue, dried, weighed, using :

	(Grammes.)
50 c. c. Pepsin Solution + 50 c. c. Solution I.....	1.045
“ “ + 50 c. c. Solution II.....	1.020
“ “ + 50 c. c. Solution III.....	0.935
“ “ + 50 c. c. water.....	0.770

Since the 10 grammes of moist albumen dried at same temperature yielded 1.265 grammes of dry albumen we have dry albumen dissolved under same conditions of experiment.

	(Grammes.
By use of Solution I.....	0.220
“ “ II.....	0.245
“ “ III.....	0.330
“ “ Water.....	0.495

from which it follows that the action of the lactates and tartrates is almost precisely the same, while the soluble constituents in a corresponding strength of alum baking powder exhibit a less retarding action on digestion. The reason that only the soluble constituents in alum baking powder residue were employed was that if the insoluble residue were also employed what remained undissolved by the hydrochloric acid and pepsin solution would vitiate the result on the undissolved albumen.

A second series of experiments was now tried in precisely the same manner, but employing the residue from an alum phosphate powder. This was made up as follows, being an average formula for this class of powders and again taking 40 grains ( $2\frac{4}{10}$  grammes) of sodium bicarbonate :

Sodium bicarbonate.....	$2\frac{4}{10}$ grammes
Burnt ammonia alum.....	$1\frac{4}{10}$ “
Acid calcium phosphate.....	$2\frac{7}{10}$ “
(Commercial powder).	

This was dissolved in water, filtered and the filtrate made up to 250 c. c., and, as before, one-fifth ( $\frac{1}{5}$ ) was taken in the experiments. We call this Solution IV.

In the Journal of the American Chem. Soc., 9, No. 2, will be found the reasons for considering that about one-sixth ( $\frac{1}{6}$ ) of the alumina present in such a baking powder is dissolved in stomachic digestion and so effects the action of the gastric juice. We have therefore to add to the 50 c. c. of Solution IV. the amount of alumina which would be soluble in the gastric juice, and which was insoluble in the water solution made. This would amount to 47 milligrammes of the burnt alum, using the factor



for solubility already quoted ( $1\frac{1}{2}$  grammes  $\times \frac{1}{2} \times \frac{1}{2} = 47$  milligrammes).

In the new experiments the conditions were the same as in the first set, except that the residues employed were from the alum phosphate powder 50 c. c. of the plain water solution in the one case (Sol. IV.), and in the other, 50 c. c., with the addition of 47 milligrammes of burnt alum. As before, a corresponding quantity of the residue from a cream tartar powder was employed for comparison. The results obtained were as follows :

10 grms. of albumen dried = 1.310 grm. dry substance.

Undissolved residue of albumen, dried, using :

	(grammes.
50 c. c. Pepsin Solution + 50 c. c. of Solution IV....	1.040
“ “ + 50 c. c. of Solution I.....	1.065
“ “ + 50 c. c. of Solution IV,	
+ 0.047 grm. burnt alum.....	1.065
50 c. c. Pepsin Solution + 50 c. c. Water.....	0.900

Showing that under the same conditions of the experiment the amount of dried albumen dissolved was with :

	(grammes.
Pepsin solution and water.....	0.410
“ “ “ Solution IV.....	0.270
“ “ “ Solution I.....	0.245
“ “ “ Solution IV. + alum .....	0.245

It would thus appear that with the ordinary formula used for alum phosphate baking powders as manufactured in this country, the inhibitory action on stomachic digestion of the various residues is practically the same for the same leavening effect whether a cream of tartar powder, an alum phosphate powder or the old method of sour milk and soda is employed.

## A NEW METHOD FOR THE DETERMINATION OF VAPOR DENSITIES.

BY EDW. GUDEMAN.

The principal on which this new modification of the Victor Meyer method consists, is the adding of an indifferent second substance to the one under the examination. The added substance is one which has a boiling point some 10-30° C. below the body whose vapor density is to be determined.

The effect, due to the addition of the second body, is the same as produced by a partial vacuum. Decomposition is, in many cases prevented, as the temperature required for the determination need in no case be above the boiling point of the body under examination. In many cases, the correct results can be obtained 10-20 degrees C. below the boiling points of the bodies examined.

Experiments were made with mixtures of :

Acetic acid and toluol.

Toluol and benzol.

Naphthalene and p-toluidine.

Diazobenzolimid and pseudocumol.

Nicotine and naphthalene.

Nicotine and p-toluidine.

Phenyldiazosulphide and naphthalene.

Phenyldiazosulphide and p-toluidine.

Chloral hydrate and benzol.

The observations were made at temperatures below and at the boiling points of the substances mentioned.

The results so far obtained are satisfactory, but as the experiments are still being continued, a detailed account will not appear until some future time.

*School of Mines, Columbia College, October 3, 1890.*

## SYNTHESES IN THE SUGAR GROUP.

BY EMIL FISCHER.

Translated by L. H. Friedburg, Ph. D.

(Continued from page 348.)

On heating dulcite with dilute nitric acid Carlet<sup>1</sup> obtained a liquid which strongly reduced alkaline copper solution, and which turned yellow with alkalies.

Gorup-Besanez<sup>2</sup> studied this process more thoroughly a year later with mannite. As an oxidizer he used platinum sponge and atmospheric oxygen and thus obtained an amorphous, fermentable sugar, the so called mannitose, which, however, was said to differ from the natural compound by optical inactivity.

Twenty-three years later the interesting experiment of Gorup-Besanez was repeated with better facilities by Dafert.<sup>3</sup> He concluded that manitose is a mixture of fruit sugar with other unknown products, the isolation of which he found to be impossible.

Aided by the new reagent I studied anew the oxidation of mannite in 1887. Using dilute nitric acid, I obtained, along with fruit sugar, a second sugar, which in contrast to the then known compounds, furnished a difficultly soluble hydrazone. This is the previously mentioned mannose. A further research which I undertook together with Dr. Hirschberger, lead to the surprising result that it possesses the same structure as glucose, that it is the real aldehyde of mannite, while glucose belongs to a stereoisomeric series.<sup>4</sup> Mannose was thus originally an artificial product, but it soon was found in plants. Tollens and Gans<sup>5</sup> obtained it by hydrolysis of salep mucous, and R. Reiss<sup>6</sup> as a product of

<sup>1</sup> Jahresbericht für Chemie, 1860, 250.

<sup>2</sup> Ann. Chem. Pharm., 118, 257.

<sup>3</sup> Ber. d. chem. Ges., 17, 227, and Zeitschrift des Vereins für Rübenzucker-Industrie, 1884.

<sup>4</sup> Ber. d. chem. Ges., 22, 574.

<sup>5</sup> Ann. Chem. Pharm., 249, 256.

<sup>6</sup> Ber. d. chem. Ges., 22, 609; 22, 3218.

decomposition of the so called reserve cellulose. This latter is found in sundry palm fruits, particularly in the corocos nut (Steinnuss). The shavings which result in the manufacture of buttons from this nut offer a cheap and ample raw material for obtaining this sugar.

The knowledge of mannose has been of particular influence in the study of the sugar group; the observation that mannonic acid, formed from this sugar, is the optical isomere of arabinose carbo acid, furnished the key for the understanding of the mannite group. I shall recur later to this point.

As with dulcete and mannite we find also that the simpler polyatomic alcohols erythrite and glycerol, when cautiously oxidized, furnish sugar-like products. Dr. Tafel and myself have called these erythrose and glycerose<sup>1</sup>, and we have isolated them as beautifully crystallizing osazones. Our publication caused a reclamation on the part of Grimaux<sup>2</sup> who says, that he had reported upon the preparation of glycerol aldehyde and its property of fermenting with beer yeast, a year previous, in the protocol of the meeting of the Chemical Society of Paris. But he did not succeed in isolating the product nor in proving that it was glycerol aldehyde for want of suitable methods.

In regard to all this I must draw attention to a much older, almost forgotten notice of I. van Deen<sup>3</sup> from the year 1863. He observed that a substance is formed from glycerol by nitric acid as well as by electrolysis, which strongly reduces alkaline copper solution and which admits of fermentation. His statement that this substance is a crystallizable sugar has been disputed from different sides, but no one has contradicted the formation of this reducing substance. Since now our own experiments as well as those of Grimaux confirm the data of van Deen in this direction, he must be considered the first observer of glycerose.

Although the proof that this is a derivative of glycerol of the formula  $C_3H_6O_3$  has only been furnished by us by means of ana-

<sup>1</sup> *Ber. d. Chem. Ges.*, **20**, 1088.

<sup>2</sup> *Compt. Rend.*, **104**, 1276; *Ber. d. Chem. Ges.*, **20**, 3384.

<sup>3</sup> *Jahresbericht f. Chem.*, **1863**, 501; also *Tydschrift voor Geneeskunde*, **4** and **5**.

lysis of the osazone even this result does not yet decide the question, whether this product is the aldehyde or the ketone of glycerol, since both must furnish the same osazone. On the contrary we were only able to conclude much later that glycerose is to be considered a mixture of both by the following observations: Dilute alkali transforms the substance into sugars containing along with other products  $\alpha$ -acrose (of which we treat later) which requires for its formation glycerol aldehyde.<sup>10</sup>

Furthermore glycerose combines with hydrocyanic acid forming an intermediary cyanhydrin, which on saponification gave us trioxymisobutyric acid, which can only form from the ketone, *i. e.* the dioxyacetone.<sup>11</sup>

The easiest manner of obtaining glycerose is that of oxidation of glycerol with bromine and sodium carbonate. This mode is particularly adapted for a lecture experiment. To this end dissolve 10 grms. glycerol and 35 grms. crystallized soda in 60 grms. warm water, cool to the temperature of the room and add 15 grms. bromine. This latter dissolves on shaking and the development of  $\text{CO}_2$  begins at once. The reaction is only finished in half an hour, but already in two minutes the formation of glycerose can be proven. Take out a sample of the liquid, saturate it with  $\text{SO}_2$  until discolored, so as to destroy hypobromic acid, then saturate with alkali and finally add Fehling's solution. Now, on heating, coloration to red and separation of cuprous oxide takes place.

In the same manner the change of mannite into laevulose can be shown.<sup>12</sup>

The purest glycerose, comparatively, is obtained by action of bromine vapor upon the lead compound of glycerol<sup>13</sup>; but the greater part of the product thus gained consists of dioxyacetone. The preparation of pure glycerol aldehyde has so far remained an unsolved problem of no inferior interest.

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<sup>10</sup> *Ber. d. Chem. Ges.*, **20**, 3385.

<sup>11</sup> *Ber. d. chem. Ges.*, **22**, 106.

<sup>12</sup> Dissolve 5 grms. mannite and 12 grms. soda in 40 grms. water. After cooling add 5 grms. bromine.

<sup>13</sup> *Ber. d. chem. Ges.*, **21**, 2635.

All the experiments so far reported upon were merely antecedents for the synthesis of natural sugars. The final aim of the research has gradually forced them into existence. In approaching now this final aim, I have at first to draw your attention to some historical data.

The thought of preparing glucose artificially is as old as organic synthesis itself.

Liebig and others have often pointed to the importance of this problem and many a note of the older literature puts it beyond doubt that earnest endeavor to realize this idea was made. But if we adhere to the principle that in working at such tasks, only the actual success signalizes an advance of science, then the history of sugar synthesis begins only 29 years ago with the discovery of methylenitane by Butlerow.<sup>14</sup> He obtained it by cautious addition of lime water to a hot solution of trioxymethylene, the polymere of formaldehyd. He describes it as a faintly yellow syrup of sweet taste, which shows the ordinary sugar reactions, but being optically inactive and seemingly not fermentable with beer yeast. He believes it possible as a preliminary step to express the composition of the product by the formula  $C_7H_{14}O_6$ , but he remarks that the analyses of the syrup yielded varying results. Butlerow was by no means in doubt about the importance of his observation, for he concludes his short but memorable paper with this sentence: "And if so we can say that here we have the first example of the total synthesis of a body of sugar like nature."

General attention seems only to have been attracted by this experiment of Butlerow after A. von Baeyer<sup>15</sup> had applied it as the basis of his well known hypothesis in regard to the formation of sugar in plants. Now the experiment was repeated from different sides, but without yielding noticeable results.

The work of Oskar Löw<sup>16</sup> shows an advance of this remarkable synthesis. By means of a modification of A. W. von Hofmann's method, he furnished an easy and productive method for the

<sup>14</sup> *Ann. Chem. Pharm.*, **120**, 295; *Compt. Rend.*, **53**, 145.

<sup>15</sup> *Ber. d. chem. Ges.*, **3**, 67.

<sup>16</sup> *Journ. für prakt. Chem.*, **33**, 321.

preparation of formaldehyd<sup>17</sup>, thus offering to himself and others the possibility of studying its condensation in a larger measure. He then showed that the transformation of the aldehyd into sugar by lime water takes place even at ordinary temperature. He called the sweet syrup thus prepared formose, with the formula  $C_6H_{12}O_6$ . He pronounced it to be different from methylenitane, which at the utmost contained but twenty per cent. formose, in addition to the products of decomposition of this sugar. Unfortunately, Löw, in his conclusions, overstepped the limit of his observations, and thus his statement that formose differs from methylenitane and is to be considered as the first artificial sugar called forth vigorous contradiction, especially from Tollens.

As methylenitane formose neither ferments with yeast, nor furnishes laevulinic acid with hydrochloric acid, the formula  $C_6H_{12}O_6$  which Löw chose was not sufficiently proven, since the analyses of such a syrup are not decisive and furthermore the only crystalline derivative of formose, the osazone should (according to Löw's analyses) not possess the formula  $C_{18}H_{22}N_4O_4$ , but that of  $C_{18}H_{22}N_4O_3$ . If the former had been correct, formose ought to have been represented by the formula  $C_6H_{12}O_5$  and thus would have been considered as an isomere of rhamnose. This contradiction in Löw's work led me to repeat his and Butlerow's experiments and to scrutinize them with the aid of phenylhydrazin<sup>18</sup>.

Then it appeared that methylenitane and formose are essentially the same, *i. e.*, mixtures of different sugar like compounds.

In both cases the main product is a sugar which really has the formula  $C_6H_{12}O_6$  as an expression. Its osazone melts near  $144^\circ$ , and has the normal composition  $C_{18}H_{22}N_4O_4$ . For this compound (which, by the way, shows but a very slight similarity to glucose) the well chosen name of "formose" may be maintained.

On this occasion also was observed another sugar, of much more interest, which is contained in small quantity in the product of condensation of formaldehyde. Its osazone showed great similar-

<sup>17</sup> Compare: Tollens, *Ber. d. Chem. Ges.*, 19, 2143.

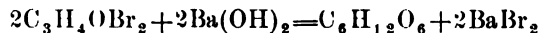
<sup>18</sup> *Ber. d. Chem. Ges.*, 21, 989.

ity, in melting point and solubility, with glucosazone. Later on it was identified with  $\alpha$ -acrosazone.<sup>19</sup>

Immediately after publication of this last observation, O. Löw<sup>20</sup> reported upon a new method of condensation of formaldehyde. On warming its dilute watery solution with lead and magnesium oxide, he obtained a syrupy sugar, which was directly fermentable. But even this product, which Löw calls methose is nothing else than  $\alpha$ -acrose, as the more minute study of the osazone showed. But in this case it is formed in greater quantity, as in the case of condensation with lime, and for this reason the raw product is directly fermentable.

In the meantime (1887) the discovery of the acroses<sup>21</sup> was made, which gave to all my work a determined direction. As we have already seen, acrolein bromide is transformed by bases into a product of the nature of sugar.

For a lecture experiment it suffices to agitate a few drops of the bromide with strongly diluted, cold sodic hydrate solution, and to test the filtrate of the separated resin with Fehling's solution. The study of this phenomenon led Dr. Tafel and myself to the discovery of the acroses. They are formed in considerable quantity only by very cautious decomposition of the bromide, by means of cold baryta water. The formation of sugar then takes place according to the equation :



The isolation of the sugar can only be perfected by its transformation into the osazone. We were thus enabled to prove that this reaction furnishes, along with other still unknown products, two isomeric sugars,  $\text{C}_6\text{H}_{12}\text{O}_6$ , which were distinguished as  $\alpha$ - and  $\beta$ -acrose.

The preparation of these two compounds from glycerose<sup>22</sup> is far easier, since even dilute alkali in the cold condenses it to sugar. It is merely necessary to take the solution of glycerose, as shown

<sup>19</sup> *Ber. d. chem. Ges.*, **22**, 359.

<sup>20</sup> *Ber. d. chem. Ges.*, **22**, 475.

<sup>21</sup> *Ber. d. chem. Ges.*, **20**, 1093, 2566.

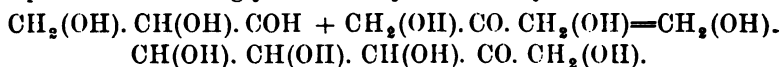
<sup>22</sup> *Ber. d. chem. Ges.*, **20**, 3384.



to be prepared by the action of bromine and soda upon glycerol, to just supersaturate it by means of caustic soda solution and to allow it to rest for two days at 0°. Thus all glycerose will be transformed into sugar. The process corresponds to the empirical equation:  $2 \text{C}_3\text{H}_6\text{O}_3 = \text{C}_6\text{H}_{12}\text{O}_6$ .

Here also several sugarlike compounds are formed, of which only the two acroses were isolated in form of osazones.

The  $\alpha$ -acrose, which here also is only formed in small quantity, is generated most likely according to the aldol formation from equal molecules of glycerol aldehyd and dioxyceton.



The reaction takes place under conditions which are also given in the plant, and consequently it is much more interesting, from a physiological standpoint than the formation of sugar from acrolein bromide. The same remark obtains still more fully for the above mentioned transformation of formaldehyd into  $\alpha$ -acrose.

The properties of  $\alpha$ -acrosazone attract closer attention, since it is deceptively similar to glucosazone, from which it differs essentially only by its optical inactivity. The surmise, therefore, which later on developed into certainty, that  $\alpha$ -acrose is the inactive form of glucose or laevulose was soon suggested. Nevertheless, it required the work of years to pass from acrose to natural sugars.

The first and greatest difficulty was offered by the re-transformation of  $\alpha$ -acrosazone into the sugar. It was only accomplished in a satisfactory manner, after the above method had been found, by which we pass from glucosazone, by way of the osone, to laevulose.

If this method be applied to acrosazone a sweet syrup results, which ferments with beer yeast, forms laevulinic acid with HCl, and is transformed by sodium amalgam into a beautifully crystallizing hexatomic alcohol, the  $\alpha$ -acrit.<sup>23</sup> This latter showed such a remarkable similarity to mannite that we suspected it to be its inactive form.

<sup>23</sup> *Ber. d. chem. Ges.*, 22, 97.

Thus the way for the synthesis of natural sugars seemed to be opened. Another obstacle arose, however, in the difficulty of obtaining the raw material. If we consider that a kilo. of glycerol, in consequence of the manifold operations and the partially scant yield, furnishes but 0.2 grms. of acrit, we understand that only the rise of a factory for the manufacture of acrose could have helped us. Thus we were forced to break off our work at this point and look for another method.

In order to show what fortunate accidents sometimes lead to success I shall have to return to the natural sugars.

Mannose is the aldehyd of mannit and is consequently transformed by bromine water into the monobasic mannonic acid:  $C_6H_{12}O_7$ . It had to be considered that such a simple reaction could not be troublesome. But the other products of oxidation prevent the acid from crystallizing. The same is to be said of the corresponding salts and thus in order merely to purify this acid a new method had to be discovered. Here also phenylhydrazin was of assistance. It forms with the acids of the sugar group, when warmed in aqueous solution, well crystallizing hydrazides<sup>24</sup>, from which by splitting with baryta water the acid is easily regenerated. The aqueous solution of the thus purified mannonic acid<sup>25</sup> when evaporated is transformed into the well-crystallizing lactone:  $C_6H_{10}O_6$ . A compound of the same composition had been found some years previously by Kiliani<sup>26</sup> when aggregating hydrocyanic acid to arabinose. Both lactones are remarkably similar, but they turn the polarized ray in a different sense and, in aqueous solution combine with each other to a third, inactive compound<sup>27</sup>.

Evidently they offer an analogue to dextro and laevo tartaric acids and offer the first example of this kind of isomerism in the sugar group.

In order to convey the same phenomenon to the mannose, it is only necessary to transform the three lactones into sugar. This

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<sup>24</sup> Fischer & Passmore, *Ber. d. chem. Ges.*, **22**, 3728.

<sup>25</sup> Fischer & Hirschberger, *Ber. d. chem. Ges.*, **22**, 3219.

<sup>26</sup> *Ber. d. chem. Ges.*, **19**, 3034.

<sup>27</sup> *Ber. d. chem. Ges.*, **23**, 370.

is attained in a very simple manner by reduction with sodium amalgam in cold solution acidulated by sulphuric acid. This new reaction<sup>28</sup> which was of the greatest consequence in the whole research, is also easily to be demonstrated. To a cold ten per cent. aqueous solution of 3 grms. mannonic acid lactone I add alternately dilute sulphuric acid and sodium amalgam, so that the reaction remains always an acid one. If the action of the amalgam be increased by strong agitation, the experiment takes hardly more than five minutes. The liquid separated from mercury reduces Fehlings' solution vigorously and gives with phenylhydrazin acetate in the cold after a few minutes a precipitate of mannosephenylhydrazone.

In the same manner the arabinose carbo acid furnishes the isomeric laevomannose, while the third lactone permits an inactive sugar to result.

By further reduction the three sugars are transformed into three optically different mannits and thus nine compounds result which may be grouped into three optical series.

The following table, which represents all now known members of the mannit series in tabular form, contains the nine compounds in the mannose group where they are distinguished by the signs, *d*, *l* and *i* (dextro, laevo and inactive).

#### MANNITE SERIES.

l. Fructose.	i. Fructose.	d. Fructose.
—	( $\alpha$ -Acrose.)	(Fruit sugar.)
	i. Glucosone.	d. Glucosone.

#### MANNOSE GROUP.

l. Mannonic acid.	i. Mannonic acid.	d. Mannonic acid.
(Arabinose carbo-acid.)		
l. Mannose.	i. Mannose.	d. Mannose.
l. Mannite.	i. Mannite.	d. Mannite.
	( $\alpha$ -Acrit.)	
l. Mannosaccharic acid.	*i. Mannosaccharic acid.	*d. Mannosaccharic acid.
(Meta-saccharic acid.)		

<sup>28</sup> *Ber. d. chem. Ges.*, **22**, 2204 and **23**, 930.

\* The compounds marked \* are new, but they will be described as soon as possible.

## GLUCOSE GROUP.

*l. Gluconic acid.	*i. Gluconic acid.	d. Gluconic acid.
*l. Glucose.	*i. Glucose.	d. Glucose. (Grape sugar.)

## ALCOHOLS ABSENT.

*l. Saccharic acid.	*i. Saccharic acid.	d. Saccharic acid.
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Immediately underneath these we find three further compounds, which stand to each other in the same optical relation, and which are named mannosaccharic acids. The compound of the left series is Kiliani's metasaccharic acid,<sup>29</sup> prepared from arabinose carboxylic acid. The two isomeres are formed in the same manner from i and d. mannonic acid by oxidation with nitric acid. The table shows, furthermore, three sugars called fructose. The d. compound is the ordinary fruitsugar and the d. glucosone right underneath it we have seen to be formed from the ordinary glucosazone. The three other compounds of this group are products of synthesis. The new bodies of the glucose group, which also contains grape sugar, I shall recur to later.

Here we have arrived at a point where the analytical research meets the work of synthesis.

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<sup>29</sup> *Ber. d. chem. Ges.* 20, 341; 2710.

(To be Continued.)

## ABSTRACTS.

### ANALYTICAL CHEMISTRY.

#### Separation of Barium from Strontium. R. FRESSENIUS.

A continuation of the papers on the above subject published in the *Ztschr. anal. Chem.*, 29, 20-28, 143-160.

In addition to the methods there reported, the separation was attempted by precipitation as chromates and found to succeed admirably under conditions as given below :

The solubility of  $\text{Ba CrO}_4$  was found to be in

.75% ammon. acetate solution	1 pt. in 49381
1.5%       "       "       "	1 pt. in 23555
.5%       "       nitrate       "	1 pt. in 45162

showing that ammonium salts do not greatly increase the solubility of barium chromate.

Strontium chromate was found to require 831.8 parts of water for solution, or in solutions containing

.5% ammon. chloride, 1 pt. in 512

.1% acetic acid, 1 pt. in 63.7

.75% am. acetate, 4 drops acetic acid and 6 drops chromate solution, 1 pt. in 348.8.

For carrying out the method of separation the following solutions were used :

1. Solution of ammon. chromate containing 0.1 grm am. chromate, pure (prepared from pure am. bichromate, neutralized with sufficient ammonia to leave the solution just slightly acid).

2. Ammon. acetate 0.31 g per c.c.

3. Acetic acid of 1.065 Sp. Gr.

4. Nitric acid of 1.20 Sp. Gr.

The mixture for separation contained the equivalent of 0.2774 g Ba and 0.4864g Sr. in the form of chlorides. The solution was

diluted to 300 c.c. and 6 drops of acetic acid added ; the solution then heated and while hot precipitated with 10 c.c (or an excess) of am. chromate. After one hour the precipitate was washed by decantation with water containing am. chromate until the filtrate gave no precipitate with ammonia and am. carbonate solution. 100 c.c. water were used in washing. The precipitate was then washed with pure water (110 c.c.) until the washings gave but a faint brownish red color with  $\text{AgNO}_3$  solution. The precipitate was next removed to a capsule. Portions remaining on the filter through which the liquid was decanted were dissolved in a little nitric acid and washed into the capsule containing the bulk of the precipitate ; a little more nitric acid was added (2 c.c. used in all) so as to completely dissolve the precipitate upon warming. The solution was then diluted to 200 c.c., heated 5 c.c., am. acetate sol. was gradually added, and then am. chromate solution (10 c.c. required) until the smell of acetic acid disappeared. After one hour the liquid was poured through a filter, (ac filter) hot water was added to the precipitate and, after cooling, the liquid was decanted, the precipitate transferred to the filter and the washing with cold water was continued until the washings no longer reacted with  $\text{AgNO}_3$  solution. The precipitate thus obtained, after gentle ignition, showed a yield of 99.78% of the barium taken. The precipitate was free from strontium. The various filtrates and washings containing the strontium were collected, 1 c.c. of nitric acid was added, the liquid was concentrated, and then precipitated hot with ammonia and am. carbonate. The precipitated carbonate, after washing, was dissolved in hydrochloric acid, alcohol was added and the strontium was precipitated by sulphuric acid. The strontium thus recovered indicated 100.25%, showing that the separation under the above conditions was perfectly practicable. The author summarizes the results of his investigation as follows :

1. Barium chromate is insoluble in water containing acetic acid when so much am. chromate is present that the solution contains only am. acetate and bichromate.
2. Barium chromate dried at  $110^\circ \text{C}$  is not dry, but still contains about 0.5% of water.
3. Gentle ignition does not decompose  $\text{BaCrO}_4$ .

4. Estimation of barium by precipitation with am. chromate gives satisfactory results. (The conclusions of 1, 3 and 4 verify those of *Schweitzer*.)

5. A complete and satisfactory separation of barium from strontium is possible by double precipitation as chromates under the above conditions. (*Ztschr. anal. Chem.*, **29**, 413-430.)

J. F. G.

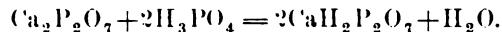
**Estimation of Water in Superphosphates.** JULIUS STOKLASA.

The author obtained some very interesting results in drying superphosphates. In determining the influence of temperature upon mono-calcium phosphate a pure crystalline salt of the following composition was used :

CaO .....	22.36%
P <sub>2</sub> O <sub>5</sub> .....	56.67%
H <sub>2</sub> O .....	21.53%
Free P <sub>2</sub> O <sub>5</sub> .....	0.014%

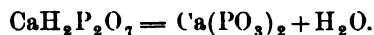
Upon drying at 100° C. this salt lost 1.83%, 2.46%, 5.21%, 6.32%, 6.43% of water respectively in 10, 20, 30, 40, 50 hours. The loss of 6.43% remained constant and is equivalent to one molecule of water. CaH<sub>4</sub>(PO<sub>4</sub>)<sub>2</sub> therefore loses all of its water of crystallization only after 40 hours drying if dried at 100° C., resulting in opaque, non-hygroscopic crystals, which dissolve slowly in 200 parts of water without decomposition.

The temperature may reach 105° C. without causing any further material change in the crystals, but if continued for 20 hours decomposition sets in. At higher temperatures, up to 200° C., decomposition is very rapid, resulting in the formation in part of free phosphoric acid, mono-calcium pyrophosphate, pyro-, and meta-phosphate. Drying at 200° for 1 hour results only in mixtures of the above compounds. At high temperatures the free P<sub>2</sub>O<sub>5</sub> probably reacts upon the normal calcium pyrophosphate and forms mono-calcium pyrophosphate.

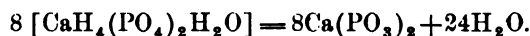


The height of the temperature and the length of time of drying at 150° C. or over, influences greatly the formation of monocal-

cium pyrophosphate. The latter salt when dried at 210° C. loses 1 molecule of water and is completely changed to calcium metaphosphate.



If the drying of monocalcium phosphate is conducted at 210° C. all the various changes may be summarized in the formation of calcium metaphosphate as follows:



(*Ztschr. anal. Chem.*, **29**, 390-397.)

J. F. G.

#### Water Analysis. By DR. DICKMAN.

The author, having found diphenylamin in a water contaminated with the waste waters from gas works, suggests the test for diphenylamin as a supplementary reaction for ascertaining such pollution. If diphenylamin is present, the residue of such a water will give the characteristic blue color with dilute sulphuric acid, the nitrates in the water being sufficient (?) to bring out the reaction. (*Ztschr. anal. Chem.*, **29**, 398.)

J. F. G.

#### Rise of Freezing Point in Thermometers. By F. AL- LIHN.

The author, in testing quicksilver thermometers made of glass from Jena and Thüringen, found that the scale of the former was less subject to change than the latter, and recommends that to prevent the rising of the freezing point, the glass, before fixing the scale, be heated to 300° C. for thirty hours. (*Ztschr. anal. Chem.*, **29**, 381-390.)

J. F. G.

#### Adulteration of Thomas Slag. By L. BLUM.

The direct admixture of foreign phosphate is difficult to detect, but inasmuch as the phosphates which can be profitably used for the purpose are usually very rich in  $\text{CaCO}_3$ , any Thomas slag which will yield a very notable quantity of  $\text{CO}_2$  should be looked upon with suspicion. Thomas slag may absorb  $\text{CO}_2$  on account of



the full CaO contained in the same, but the quantity thus absorbed is not likely to exceed 2.5%. A dry Thomas slag which, upon ignition, loses over 2% in weight, should be examined as to the per cent. of CO<sub>2</sub>. (*Ztschr. anal. Chem.*, **29**, 408-411.)

J. F. G.

**Determination of Bile Constituents in Urine.** ADOLF JOLLES.

Urines before and after dilution were subjected to the tests of Gmelin, Huppert, Vitali, Rosenbach, Ultzman, Hoppe-Seyler, Dragendorff, and to the process of extracting the urine with chloroform and subjecting the chloroform solution to the action of nitric acid or bromine water by which the color rings are developed. Of these the two following methods were found to be the most satisfactory :

Rosenbach's test was modified somewhat by passing a large quantity of urine through a pure white filter paper, then dropping upon the inner surface of the paper a drop of nitric acid containing a little nitrous acid, after which the funnel holding the paper was gently warmed by passing it over a Bunsen's flame 3 or 4 times. The gentle heating makes the test more delicate, so that mere traces of bile pigments are indicated by the appearance of a bright green ring around the drop of nitric acid.

The delicacy of Huppert's test was found to depend much upon the concentration of the "lime water." A solution containing 10.g CaO per litre is the most suitable.

Take 8 to 10 c.c. urine, add an equal volume of the lime water, shake the mixture and filter. Wash the precipitate into a small beaker with alcohol and dilute hydrochloric acid, filter and boil the filtrate. If bile pigments are present the filtrate will turn green to blue. For determining approximately the relative quantity of bile constituents excreted the iodine number is suggested.

The iodine number is calculated from the formula  $I = \frac{g}{s-1} \cdot 4.292$ , in

which  $g$  = grms. of I, which 10 c.c. urine absorb and  $s$  the sp. gr. of the urine. Urine free from bile constituents was found to require not over 7.3 to 7.8 of I, while in specimens containing bile

constituents the iodine numbers varied from 6.5 to 17.4, the iodine number increasing proportionately with the quantity of bile constituents. (*Ztschr. anal. Chem.*, **29**, 402-406.)

J. F. G.

**A New Test for Albumen.** ADOLF JOLLES.

Mix 8 to 10 c. c. of urine with an equal volume of concentrated hydrochloric acid; then carefully add two or three drops of a saturated solution of "chloride of lime," so that it will form a supernatant layer. If the urine contains albumen, a white turbidity will appear at the junction of the two layers. The test will clearly show the presence of  $\frac{1}{1000}$ % of albumen, and although it is less sensitive than the nitric acid test (it will indicate 0.00015 grm. albumen in 100 c. c.), the two together are very useful for clinical purposes. Thus if the "chloride of lime" test fails to indicate albumen while the nitric test does, then it is safe to assume that the urine contains less than  $\frac{1}{1000}$ % albumen. If both tests should indicate albumen, the urine may be diluted to some definite volume, until the "chloride of lime" test just fails to indicate albumen. By making the necessary calculation for the change of volume, the quantity of albumen may be approximately determined. (*Ztschr. anal. Chem.*, **29**, 407.)

J. F. G.

**Determination Albumen in Bacterial Urine.** ADOLF JOLLES.

For indicating mere traces of albumen the  $K_4FeCy_6$  test is the most delicate, as it will detect even 0.0008 grm. albumen in 100 c. c. of urine. The urine must be filtered perfectly clear. Acetic acid and  $K_4FeCy_6$  solution are then added, and any turbidity noted. Urine containing bacteria should be shaken with kieselguhr\* (infusorial earth), after which the urine will filter clear. (*Ztschr. anal. Chem.*, **29**, 407.)

J. F. G.

\* Finely divided asbestos fibre, ground to a pulp, will answer the purpose equally well.

J. F. G.

## Abstracts of American Patents Relating to Chemistry.

(From the U. S. Patent Office Gazette.)

(Issued September 30, 1890.)

**487,192.**—Absorber for refrigerative apparatus. P. R. Gray, Jr.

**487,193.**—Still. P. R. Gray, Jr.

**487,252.**—Sulphur candle. C. H. Shaw.

Consists of a block of sulphur provided with a wick.

**487,258.**—Composition for lining barrels. M. E. Spofford.

Consists of wood ash lye, essential oil and resin, glue, molasses and starch.

**487,265.**—Process of manufacturing copper. H. H. Vivian.

The copper-containing material is treated with an organic acid, and then reduced to the metallic state.

**487,295.**—Mordant. E. O. Frankhauser.

Consists of castor oil, sulphuric acid, soda lye, ammonia, white soap and sumach.

**487,306.**—Process of etching on lithographic stones or zinc. F. Kraupa and L. Moser.

The stone or plate bearing the design is sprinkled with finely powdered rosin, then rubbed with talc, and then covered first with a sheet of paper saturated with alcohol and then with a layer of damp paper. The rosin forms a crust which resists the action of the etching fluids.

**487,315.**—Apparatus for producing gas from hydrocarbon oil. J. McKay.

**487,356.**—Process of testing liquids. T. Clement.

**487,421.**—Apparatus for refining oil. C. Dorn and J. Carey.

**487,433.**—Water filter. H. Hegner and J. M. Skinner.

**487,443.**—Filter. E. Mertz.

**487,448.**—Apparatus for making soap. M. J. Palmer.

**487,454.**—Carburetor. D. D. Ranney.

**487,499.**—Explosive compound. D. Mindeleff.

Consists of nitroglycerine, and alcohol, and a soluble explosive.

**487,525.**—Artificial building stone. A. von Solemacher-Antweiler.

100 parts silica, 5 parts fluor spar, 5 parts feldspar, 20 parts soda, 5 parts tin ash, 5 parts alum earth, 5 parts red lead, 2.5 parts talc, and 2.5 parts

cryolite ore melted together in a regenerative glass melting furnace, at a temperature of 1500–2000°, and cast.

**487,588.**—Ink. W. G. Fuerth.

Consists of vaseline, linseed oil, and coloring matter.

**487,611.**—Gas retort furnace. K. M. Mitchell.

**487,638.**—Indigo solution. A. Ashworth.

A solution for reducing indigo is prepared by saturating a solution of sodium bisulphite with metal filings, separating the liquor, adding sodium sulphide till the formation of a precipitate ceases, filtering and adding caustic soda.

**487,659.**—Apparatus for refining oil. E. Noppel.

*(Issued October 7, 1890.)*

**487,701.**—Process of manufacturing lead pigments. G. T. Lewis.

Sublimed lead pigments containing zinc are purified by washing with water containing sulphuric or sulphurous acid.

**487,780.**—Printing or stamping ink. C. M. Higgins.

Consists of a solution of a coloring matter in oleic acid.

**487,798.**—Process of hardening steel. B. M. Pickett.

The process consists in heating steel to a red heat and then plunging it into a bath composed of a diluent and a base containing a calcined oxide or carbonate, or both of a metal of the "iron group," together with a combustible organic substance which is soluble in water, such as glucose.

**487,794.**—Process of and composition for tempering. B. M. Pickett.

**487,795.**—Composition of fluids for tempering steel. B. M. Pickett.

**487,902.**—Shavings for vinegar generators and for clarifying beer. R. H. Herder.

**487,989.**—Greenish blue dye. A. Herrmann.

The sulphonic acid of methylated and ethylated meta-amidotetralkyl-diamidotriphenyl carbinol.

**488,013.**—Process of and apparatus for the manufacture of gas. B. Loomis.

**488,053.**—Violet dye. H. Boedeker.

Is obtained by the action of sulphuric acid upon ortho- or para-ditolyl-rhodamine, produced by the action of fluoresceine chloride upon ortho- or para-toluidine. It has the characteristic properties that in form of its free acid it dissolves easily in hot alcohol, with difficulty in hot water, and with great difficulty in cold water. With alkalies it forms salts soluble in water. It dyes silk and wool violet.

**488,071.**—Apparatus for making gas from oil and steam. E. R. Ellsworth.

**488,117.**—Method of purifying lead or alloys thereof. W. Shapleigh.

The molten metal or alloy is mixed with sodium or potassium or an alloy

of these metals in sufficient quantity to deoxidize the mass, whereby the oxygen is removed and a film or coating of caustic alkali is formed, which serves to protect the surface of the molten metal.

*(Issued October 14th, 1890.)*

**488,149.**—Carboys for Acids. J. W. Fox.

**488,218.**—Gas Generating Apparatus. W. S. Wright.

**488,266.**—Vacuum Evaporating Apparatus. H. S. Firman.

**488,333.**—Process of Obtaining Meat Extracts. J. Van Ruymbeke.

**488,488.**—Manufacture of Dye Stuffs. R. Lanch and C. Krekeler.

Is produced by the combination of the diazo compound of amido-salicylic acid with alphanaphthylamine, again diazotizing the amido-azo compound obtained and recombining the diazo compound obtained with alphanaphthol-sulpho acid. It forms a blue black paste and in the dry state a blue black powder, is difficultly soluble in cold water, easily in hot water with a blue violet color, which color changes to green blue on addition of soda lye. It is precipitated from its aqueous solution by mineral acids.

**488,595.**—Rubber Compound. W. H. Allen.

Consists of rubber, sulphur and lithargite (pulverized calcined magnesium silicate.)

*(Issued October 21st, 1890.)*

**488,621.**—Paint. W. A. Hall.

Consists of hydrous magnesium silicate, dextrin, calcined plaster, powdered alum, and salt, combined with hot water, and suitable pigments.

**488,648.**—Manufacture of Fertilizers. P. B. Rose.

Stick or other albuminoid is evaporated to dryness with an insoluble compound of iron.

**488,715.**—Process of eliminating graphitic carbon from cast iron. J. B. Renshaw.

Vegetable fibre mixed with pulverized ferric oxide is added to the iron to be melted.

**488,772.**—Apparatus for recovering alkali. H. Burgess.

**488,816.**—Manufacture of explosives. C. O. Lundholm and J. Sayers.

A process for incorporating together cellulose nitro derivatives and nitroglycerin, consisting in suspending the ingredients in a liquid or water, which is incapable of dissolving them, agitating them together in the liquid, and subsequently separating the liquid.

**488,993.**—Extract of tobacco. H. Endemann.

A sheep wash produced from tobacco by extraction with acidulated water, and from which the phosphates of the alkaline earths have been removed by precipitation with an alkaline substance.

(Issued October 28th, 1890.)

**439,137.**—Process of Vulcanizing Rubber. F. G. Fowler.

**439,144.**—Curing Meats. J. H. Greenstreet.

Fresh meat is treated with a solution of soda, before being salted in the ordinary manner.

**439,150.**—Process of Manufacturing Anti-corrosive Compounds. P. Helbig and H. Bertling.

Molten lead is repeatedly poured into cotton seed oil, until the oil has absorbed the desired quantity of lead.

**439,267.**—Baking Powder or Preparation. C. A. Catlin.

Contains a salt of a fatty acid of an inorganic base as a diluent.

**439,318.**—Dry Extract of Coffee and Mode of Preparing the Same. H. Barotte.

The process consists in first subjecting the coffee to dry distillation, then making an aqueous infusion from the residue, then evaporating the said infusion and drying the resulting extract, then adding to the product thus obtained the liquid distillate, and finally drying the compound.

**439,330.**—Process of and Apparatus for Decomposing Bicarbonate of Soda. L. A. Staub.

**439,394.**—Artificial Fuel. H. K. Flagler.

Consists of hydrocarbon oil, sodium nitrate, sal-niter, salt and water.

**439,455.**—Apparatus for the manufacture of Gas. H. White.

**439,461.**—Apparatus for Generating Illuminating Water Gas. J. D. Averell.

**439,515.**—Process of Refining Fat Oils. R. Hunt.

**440,288.**—Brown dye. J. Walter.

The brown coloring matter which is easily soluble in water, difficultly soluble in spirit, a little better in methyl alcohol, insoluble in benzine and ether, soluble in concentrated sulphuric acid with magenta red color; obtained by combination of metadiamines with two diazo compounds, of which one is diazotized polychromine and the other one of the diazo compounds of naphthylamine or amidoazo benzol, or amidoazotolnol.

**440,314.**—Process of preparing granulated cleaning material. F. W. Kistenmacher.

Sawdust is caused to take up a sufficient quantity of a volatile solvent.

**440,359.**—Blue dye. C. A. Mayer.

Violet coloring matters are produced by the action of nitroso derivatives of the tertiary amines on the products of condensation of tannin or its specified equivalent with the primary amines.

**440,391.**—Insulating composition. F. E. Blaisdell.

Consists of asbestos, clay, and a flux, as feldspar and borax.

**440,414.**—Process of dyeing. F. Zeman.

The method of silk dyeing, consisting in first washing the same, then

subjecting it to a dyeing bath, next drying it, then steaming it, and subjecting it to the vapor of acetic acid, next subjecting the material to a bath of sodium silicate, then subjecting it to a hot bath of sumach, logwood, and soap, until the desired color is obtained, and finally washing.

**440,456.**—Apparatus for the manufacture of gas. A. L. Allen.

**440,464.**—Apparatus for brewing beer. M. Byrne.

**440,486.**—Carburetor. J. Love.

**440,528.**—Process of and apparatus for preserving food. C. L. Bachelier.

Alimentary substances are treated in a closed vessel with a mixture of gaseous or finely divided hydrochloric acid and carbonic acid.

**440,536.**—Blue dye. R. Bohn.

The blue dye which is in the form of paste, appears to be of a dirty greenish color; when dry it can be obtained as a crystalline powder of dark color possessing a metallic lustre, the color of which may vary from violet to green; the color of the body as shown by its streak on rubbing is blue; it is but very slightly soluble in cold water, but is readily soluble in dilute alkalis, giving beautiful blue solutions; it is practically insoluble in benzine and ether, but soluble in alcohol, and the alcoholic solution is most characteristic, being reddish violet in color, and marked by a striking reddish fluorescence,

**440,539.**—Process of preparing iron ore for filters. F. Candy.

*(Issued November 4, 1890.)*

**439,639.**—Treating residues of distillation. E. M. Cook.

**439,645.**—Water filter. W. T. Floyd.

**439,717.**—Process of making lactose or milk sugar. A. A. Bennett and C. S. Boynton.

The process consists in first treating whey with calcium hydroxide or carbonate, etc., for the purpose of neutralizing the natural acid contained therein, next heating the whey and separating it from the precipitate formed by the heat, then evaporating to the consistency of syrup and treating it in this condition with alum and soda, etc., in solution, for the complete separation of the nitrogenous impurities, and finally filtering and evaporating.

**439,733.**—Process of treating sublimed lead. C. V. Petraens.

Sublimed lead pigment is treated with water or an aqueous solution of sodium chloride and dried.

**439,745.**—Apparatus for distilling oils. E. A. Edwards.

**439,756.**—Compound for preventing incrustation in boilers. W. Blackburn.

Consists of hydrocarbon oil, starch and rice.

**439,796.**—Insulating composition. T. D. Bottome.

Consists of a solution of orthosilicic acid and silicon dioxide.

**439,805.**—Process of obtaining cream of tartar. A. Martignier.

Consists in treating lyes, argols, tartar, etc. with potassium or sodium sulphate, or a mixture of the two, separating the residuum from the liquid and then precipitating from the latter the cream of tartar by the aid of sulphuric acid.

**439,834.**—Preparing pressed yeast. E. Brunn.

**439,880.**—Process of making bags acid proof. J. A. Lighthall.

Dry pulverized acid proof material in sufficient quantity to cover the interior surface of the bag is introduced into the bag, after which it is sufficiently compressed to force a portion of the acid proof material into the interstices of the fabric of which the bag is made.

**439,953.**—Process of producing azo colors on cotton or other vegetable fiber. R. Holliday.

The fiber is subjected to a mixture composed of oil, a phenol and an alkali, and dried. The dried fibre is then subjected to the action of an azo compound.

**439,970.**—Manufacture of parchmented fiber. H. W. Morrow.

**439,980.**—Vinegar apparatus. P. Spink.

**440,004.**—Apparatus for the manufacture of gas. H. Burgess,

**440,066.**—Composition of matter. C. C. Shiber.

Consists of rosin, borax, sand, cement, lime, plaster, hair, marble dust and salt.

*(Issued November 11th, 1890.)*

**440,124.**—Apparatus for recovering soda. L. D. Armstrong.

**440,139.**—Process of manufacturing and tempering steel. M. T. Coomes and A. W. Hyde.

The metal raised to a white heat is plunged into a bath composed of water, sugar, sodium chloride and ammonium chloride.

**440,143.**—Process of separating gold and platinum from other metals in solution. E. Dodé.

The process consists in subjecting the entire acid solution in the presence of ether to agitation until the ether becomes yellow, in then decanting the remaining solution from the yellow ether, in then subjecting the remaining solution to agitation in the presence of lavender until the essential oil becomes brown, and in the decanting from the brown essential oil the remaining solution and adding thereto ammonia.

**440,162.**—Chemical feeder for filters. O. H. Jewell and W. M. Jewell.

**440,173.**—Battery zinc. A. J. Macdonald.

An amalgam of mercury and ammonium is added to heated mercury, and the mercury hardened by addition of zinc. A portion of this alloy is added to the melted zinc from which battery zincs are cast. Finally some magnesium is added,



**440,232.**—Manufacture of pigments. J. C. Martin.

A combination of oxide or sulphide of zinc, hydrated calcium oxide, and a sulphate of an alkaline earth.

**440,239.**—Filtering apparatus. M. Cole.

**440,257.**—Preservative. L. Benussi and C. Dondero.

Consists of water, albumen or gelatin, potassium sulphate, sodium chloride, boric acid or sodium biborate, sodium phosphate, iron phosphate, and calcium phosphate.

**440,262.**—Apparatus for drying starch refuse, etc. P. H. Grimm.

**440,281.**—Yellow dye. C. Ris.

Obtained by treating the diazo-compound of polychromine with ammonia. It forms a light brown powder, easily soluble in water, slightly soluble in common spirits, more readily soluble in methyl alcohol, scarcely soluble in concentrated acetic acid, and insoluble in benzol and ether.

W. R.

REGULAR MEETING, NOVEMBER 7, 1890.

The minutes of the October meeting were read and accepted as read.

The following names were proposed for membership :

James E. Talmadge, D.S.D., Ph.D., Principal Latter Day Saints College, Salt Lake City, Utah.

J. A. Burns, Ph.D., Vice-Pres. and General Manager Tallapoosa Furnace Co., Tallapoosa, Ga.

S. G. Valentine, Colebrook Furnace, Lebanon, Pa.

H. F. Carpenter, Assayer, etc., 29 Page street, Providence, R. I.

W. C. Ferguson, Ph.B., Chemist Laurel Hill Chemical Works, 138 Wilson street, Brooklyn, N. Y.

Dr. J. H. Washburn, Kingston, R. I.

Harry Mullikin, Newport, R. I.

Dr. Edward P. Harris, Dept. of Chemistry, Amherst College, Amherst, Mass.

H. S. Patterson, 121 Pleasant street, Worcester, Mass.

Nathaniel J. Lane, Analytical Chemist, New York.

J. L. Perkins, " " "

J. A. Deghuée, 217 Harrison street, Brooklyn.

J. J. Tobin, U. S. N. Torpedo Station, Newport, R. I.

Harwood Huntingdon, Saylesville, R. I.

Mr. Walter M. Sanders, Hughesdale, R. I., was unanimously elected to membership.

The following papers were presented : " Note upon the Influence of Alum Phosphate Powders upon Digestion," by Lucius Pitkin, Ph. B., read by title.

"The Composition of Swill Milk," by Prof. A. R. Leeds.

"The Aeration and Composition of Niagara River Water above and below Niagara Falls," by Prof. A. R. Leeds.

"Calculation of Blast Furnace Slags," by Auguste J. Rossi, read by title.

Mr. A. Bourgouonon gave a synopsis of the last paper.

Mr. Rupp moved that the resolution adopted at the last meeting on the subject of the Philadelphia meeting be reconsidered. Carried. He then moved an amendment that the chair appoint a committee of five, of which the chairman of this meeting should be one, to take charge of the arrangements for the Philadelphia meeting. Carried. The chair named as the other members Messrs. Rupp, Chandler, Sabin, and McMurtrie. It was moved that this committee have power to enlarge their number. Seconded and carried. It was moved that the committee on the Annual Dinner be discharged and that the matter be referred to the committee of arrangements for the Philadelphia meeting. Seconded and carried.

The committee on nominations presented the official ballot for the annual election as follows:

Corresponding Secretary—A. C. Hale.

Recording Secretary—Durand Woodman.

Treasurer—F. T. King.

Librarian—William Rupp.

Curators—C. E. Munsell, J. Cawley, T. B. Stillman.

Committee on Papers and Publications—A. A. Breneman, J. F. Geisler, William Rupp.

Committee on Nominations—A. H. Sabin, A. P. Hallock, Lucius Pitkin, C. A. Doremus, J. B. Mackintosh.

Board of Directors.—Three Local Vice-Presidents, C. F. Chandler, L. H. Friedburg, R. W. Hall, A. A. Breneman, W. McMurtrie, A. C. Hale, F. T. King, E. Waller, A. H. Sabin, D. Woodman.

Advisory Council, for Three Years.—C. F. Chandler, T. G. Wormley, C. E. Monroe, J. H. Appleton.

For Two Years.—A. A. Breneman, F. A. Genth, A. B. Prescott, J. W. Mullet.

For One Year.—T. Sterry Hunt, S. W. Johnson, H. B. Nason, G. C. Caldwell.

It was moved that the order of the names presented for the Advisory Council be determined, as to tenure of office, at this meeting, by drawing by lot in two sets, the local names in one set, the non-local in another. Seconded and carried. The drawing resulted in the presentation of the names in the order given above.

The meeting was then adjourned.

CHAS. F. MCKENNA,  
Recording Secretary.

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MINUTES OF A MEETING OF THE BOARD OF DIRECTORS HELD  
NOVEMBER 6, 1890.

The meeting was held in the office of Prof. A. A. Breneman, 97 Water street, New York, and was called to order at 4:20 P. M.

Directors present were Messrs. Breneman, King, Geisler, Rupp, Kent, O'Connor and Hale.

Upon motion of Mr. Geisler, seconded by Prof. Hale, Mr. T. D. O'Connor was appointed auditor *pro tem.*, during the absence of Auditor Stebbins, now in Europe.

Upon motion of Prof. Hale, seconded by Mr. Rupp, it was declared to be the sense of the Board of Directors that all General Meetings should be regarded as *regular* meetings, and it was voted that the Board report this decision to the Society at its next regular meeting.

There being no farther business before the Board, upon motion of Prof. Hale the meeting was declared adjourned.

ALBERT C. HALE,  
Secretary *pro tem.*

## THE PERISSAD LAW.

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BY MAJOR W. R. LIVERMORE, U. S. A.

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### GENERAL OUTLINE.

The Perissad Law may be briefly explained as follows :

If the atomic weights of all chemical elements are arranged in a single ascending series, the law of increase is apparently irregular ; but almost all of these weights may be so arranged in two parallel series, that each series will show a regular law of increase as far as the atomic weights have been determined, and in almost every instance all of one series fall into those groups of classification of Mendeleyeff that indicate an even quantivalence, and almost all of the others into those indicating an uneven quantivalence.

This realizes a prediction made by Dr. J. P. Cooke in 1854, as follows :

“The doctrine of triads is, however, as I hope to be able to show in the present memoir, a partial view of this subject, since these triads are only parts of series similar in all respects to the series of homologues of organic chemistry, in which the differences between the atomic weights of the members is a multiple of some whole number.”

That paper speaks of the properties of the elements which are functions of the atomic weights, and says that “it does not seem bold theorizing to suppose that the atoms of the members of the same series are formed of a common nucleus, to which has been added one or more groups of atoms, or perhaps one or more single atoms, to which the corresponding element has not been discovered.”

At the close of his paper of 1854 Professor Cooke said : “To my conceptions, chemistry will then have become a perfect science, when all substances have been classed in series of homologues, and

when we can make a table which shall contain, not only every known substance, but also every possible one, and when by means of a few general formulæ we shall be able to express all the properties of matter, so that, when the series of substance and its place in the series are given, we shall be able to calculate, nay predict, its properties with absolute certainty."

Although Cooke and Dumas were then working with a common aim, Dumas was not so confident of this ultimate solution of the problem in hand, for in 1857 he said: "I have often tried, as Mr. Josiah Cooke has on his part, to compare them, to combine them, and to discuss them with the hope of drawing some conclusion from them with certainty, but I have been unable to draw from them anything but doubt. The formula deduced from the above simple progression,"  $(a+nd)$  "would not account for the generation of simple bodies, as Cooke had supposed." Dumas proposed a much more complicated formula, but that of Cooke is so far realized by the perissad law that out of the 54 elements embraced in the first eight series of Mendeleyeff, the atomic weights of 47 differ from the calculated value by less than three-quarters of a unit, 44 by less than half a unit, 39 by less than a third of a unit, 33 by less than a quarter of a unit, and 23 by less than a tenth of a unit.

When we consider the uncertainty in the determinations of many of those atomic weights that differ most from the regular increase, it may be admitted that Dr. Cooke's prediction has so far been verified that the formula  $(a+nd)$  has been proved to lie at the bases of all classifications of atomic weights.

These determinations are not accurate enough to justify any conclusions about the deviations from the regular increase, but in general they appear to be additive in the case of those elements that show the greatest chemical activity, and these deviations may eventually help to determine the character of molecular forces.

The periodic law of Newlands and Mendeleyeff is valuable so far as it asserts that the properties of the elements are periodic functions of their atomic weights, but unsatisfactory and perhaps erroneously stated if it is pushed so far as to assert that the number of elements in each period is identical.

The Periodic Law has, I think, never afforded any means of predicting the exact atomic weight of a new element, nor has any law been suggested to account for the marked irregularity of the Mendeleyeff series. Newlands in particular has taken great pains to call attention to its irregularity, and most of its strongest advocates believe that there is an exceedingly complex law which regulates this increase. It is the object of this paper to show that the law is exceedingly simple.

#### ARRANGEMENT OF DATA.

In tabulating the atomic weights for this discussion it is better to base it upon the lists already published rather than to prepare one for the purpose by weighing the merits of each individual determination. Although the utmost accuracy is not attained by this empirical method, it will at least be free from any coloring, which it is so hard to avoid in comparing the result of observation with the requirements of a law that has already been formulated. In the *Journal of Analytical Chemistry*, Vol. III. (1889), page 58, in an article by Venable on the atomic weights, four such lists are prepared. Table I of this paper is prepared by taking in each case from the most recent lists, viz., those of Van der Plaats and Ostwald that determination which differs least from the older ones of Clark and of Meyer and Seubert, and taking account of the subsequent determinations that have been reported in the *Journal of Analytical Chemistry* or in the *Chemical News*, by taking the mean between the new values and those taken from the lists. The standard in all the tables is  $O = 16$ .

The new determinations thus considered are as follows :

Sn=	119.1	Bongartz and Classen	(J. A. C., III., p. 93).
Zn=	65.37	Gladstone and Hibbert	(J. A. C., III., p. 350).
Cr=	52.19	S. G. Rawson	(J. A. C., III., p. 350).
Zr=	90.62	Bailey	(J. A. C., III., p. 351).
Ru=	101.66	Joly	(J. A. C., III., p. 352).
Pd=	106.51	Keiser	(J. A. C., III., p. 352).
Mg=	24.29	Burton and Vorce	(Am. Chem. J., 12, p. 219).
Cu=	63.59	T. W. Richards	(Chem. N., 59, p. 179).

The determination of the relative atomic weights of hydrogen and oxygen, although it is, perhaps, the most important of all, does not affect this table in consequence of the isolated position of hydrogen.

To adapt the formula  $a + nd$  to the series of atomic weights prepared in this manner, take the following values for  $a$  and  $d$  in the several series of common differences :

	First Series.		Second Series.	
	$a$	$d$	$a$	$d$
1st group-----	7.04	4.01	12.09	4.00
2d group-----	65.44	4.83	63.30	4.00
3d group-----	107.80	6.20	106.10	6.29

and let  $n$  represent the natural numbers 1, 2, 3, etc.

In Table I., column (2) shows the atomic weight, column (3) the difference between the successive terms of (2) ; columns (4) and (5), two parallel series of numbers in arithmetical progression, each term being placed on the line of that atomic weight which comes nearest to it in value. Column (6) shows the difference between the serial number and the atomic weight (except in the case of N, Ni and Ru, which form an independent progression with a common difference between 44 and 45 ; excepting also Be, whose apparent deviation from the law has not yet been explained, and Ge, Rh, and Ce, whose irregularity may arise from imperfect determinations of their atomic weights). Column (7) shows the number of the group in Mendeleyeff's arrangement to which each element belongs.

In Table II. the deviations from the regular increase have been arranged to correspond with the groups and series of Newlands and Mendeleyeff. The last line shows the algebraic sum of the deviations.

Plate I is a graphic representation of the series of atomic weights taken in a single series at (1) and in two parallel series at (2), (3), (4) and (5). At (6) the two parallel series are combined in one, but here the first series is represented by dots and the second series by crosses.

In (5) the asterisks represent the residual series N, Ni, and Ru.



## COMPARISON OF CALCULATED AND OBSERVED VALUES.

No regularity and no law is apparent in column (2) of Table I., or in line (1) of Plate 1. The differences in (3), Table I., range from 6.43 to 0.40. The mean of the differences is 2.79, and we find them distributed about as the theory of probability would lead us to expect from as many numbers scattered at random over the space, subject only to the condition that they should not differ by more than about 6 units from their nearest neighbors, excepting that among the lower numbers the fractions show a slight tendency to favor Prout's law. The average deviation from the mean difference is not far from 1.39 or half of 2.79.

The regularity of the double series, however, is quite apparent in Plate I., lines (2), (3), (4) and (5), and in (5) it is hard to detect with the eye that there is any irregularity whatever, excepting in the second group of the second series, viz., 63.46, 72.32, etc. From Column (6) Table I., and from Table II., it is seen that the deviations are inconsiderable. Their numerical value would average about .2, but in the lower numbers less than .1. The deviations from the two parallel series are as small as could be expected when it is considered that the four lists from which the table was prepared differ as much from each other as this series differs from the mean of all. The average range of values in the four lists would be about .3 of a unit and the new values for eight of the elements above mentioned determined within the past year, differ from those taken from the list by an average of .5 of a unit. These figures are of vital importance in their bearing on the significance of the law, which must not be classed with numerous approximate formulæ which have been suggested from time to time since the first publication of Dr. Cooke's paper in 1854.

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# THE PERISSAD LAW.

TABLE I.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
FIRST GROUPS OF PERISSAD LAW.	H.	1.00	---	-----	-----	-----	I.
		*	---	-----	-----	-----	
	Li	7.03	6.03	7.04	-----	-.01	I.
	Be	9.10	2.07	-----	-----	-----	II.
	B	11.00	1.90	11.05	-----	-.05	III.
	C	12.00	1.00	-----	12.09	-.09	IV.
	N	14.04	2.04	15.05	-----	-----	V.
	O	16.00	1.96	-----	16.09	-.09	VI.
	F	19.01	3.01	19.06	-----	-.05	VII.
	**	*	*	*	20.09	*	
	Na	23.05	4.04	23.06	-----	-.01	I.
	Mg	24.33	1.28	-----	24.09	.24	II.
	Al	27.08	2.75	27.07	-----	.01	III.
	Si	28.06	0.98	-----	28.09	-.03	IV.
	P	31.03	2.97	31.08	-----	-.05	V.
	S	32.06	1.03	-----	32.09	-.03	VI.
	Cl	35.46	3.40	35.08	-----	.38	VII.
	**	*	*	*	36.09	*	
	K	39.14	3.68	39.09	-----	.05	I.
	Ca	40.00	0.86	-----	40.09	-.09	II.
	—	-----	-----	43.10	-----	-----	
	Sc	44.08	4.08	-----	44.09	-.01	III.
	—	-----	-----	47.10	-----	-----	
	Ti	48.12	4.04	-----	48.09	.03	IV.
	V	51.30	3.18	51.11	-----	.19	V.
	Cr	52.25	0.95	-----	52.09	.16	VI.
	Mn	55.00	2.75	55.12	-----	-.12	VII.
	Fe	56.00	1.00	-----	56.09	-.09	VIII.
	Ni	58.40	2.40	-----	-----	-----	VIII.
	Co	58.80	0.40	59.13	-----	-.33	VIII.
SECOND GROUPS.	Cu	63.46	4.66	-----	63.30	.16	I.
	Zn	65.44	1.98	65.42	-----	.02	II.
	—	-----	-----	-----	67.30	-----	
	Ga	69.90	4.46	70.25	-----	-.35	III.
	Ge	72.32	2.42	-----	71.30	-----	IV.
	As	75.00	2.68	75.07	75.30	-.07	V.
	Se	79.00	4.00	-----	79.30	-.30	VI.
	Br	79.95	0.95	79.90	-----	.05	VII.
	**	*	*	*	83.30	*	
	Rb	85.44	5.49	84.72	-----	.72	I.
	Sr	87.52	2.08	-----	87.30	.22	II.
	Y	89.50	1.98	89.55	-----	-.05	III.
	Zr	90.56	1.06	-----	91.30	-.74	IV.
	Cb	94.00	3.44	94.37	-----	-.37	V.
	Mo	95.90	1.90	-----	95.30	.60	VI.

TABLE 1—*Continued.*

THIRD GROUPS.	Ru	102.33	6.43	-----	-----	-----	VIII.
	Rh	104.00	1.67	-----	-----	-----	VIII.
	Pd	106.21	2.21	-----	106.00	.21	VIII.
	Ag	107.93	1.72	107.80	-----	.13	I.
	Cd	112.08	4.15	-----	112.29	— .21	II.
	In	113.70	1.62	114.00	-----	— .30	III.
	Sn	118.50	4.80	-----	118.58	— .08	IV.
	Sb	120.00	1.50	120.20	-----	— .20	V.
	Te	125.20	5.20	-----	124.87	.33	VI.
	I.	126.86	1.66	126.40	-----	.46	VII.
	**	*	---	-----	131.16	*	
	Cs.	132.90	6.04	132.60	-----	.30	I.
	Ba	137.10	4.20	-----	137.45	— .35	II.
	La	138.50	1.40	138.80	-----	— .30	III.
	Ce	141.50	3.00	-----	143.74	-----	IV.
	Di	1 5.00	3.50	145.00	-----	.00	V.
	Sm	150.10	5.10	-----	150.03	.07	VI.

TABLE II.

*Deviations.*

Group Series.	I.	II.	III.	IV.	V.	VI.	VII.
2 ----	—01	-----	—05	—09	-----	—09	—05
3 ----	—01	+24	+01	—03	—05	—03	+38
4 ----	+05	—09	—01	+03	+19	+16	—12
5 ----	(+16)	(—02)	—35	-----	—07	—30	+05
6 ----	+72	+22	—05	—74	—37	+60	-----
7 ----	+13	—21	—30	—08	—20	+33	+46
8 ----	+30	—35	—30	-----	+00	+07	-----
Total.	+19	—03	—15	—18	—03	+11	+14

The groups and series of this table are those of Mendeleyeff's Periodic law.

For example, L. Meyer (Modern Theories, Eng. trans. p. 162), says: "An examination of the atomic weights of the following groups of elements shows the differences of the atomic weights of their members to be approximately the same.

	Dif.		Dif.	
Fe = 55.9	47.6	Ru = 103.5	95.1	Os = 198.6
Co = 58.6	45.5	Rh = 104.1	88.6	Ir = 192.7
Ni = 58.6	47.6	Pd = 106.2	88.1	Pt = 194.3
Cu = 63.2	44.5	Ag = 107.7	88.5	Au = 196.2
Zn = 64.9	46.8	Cd = 111.7	88.1	Hg = 199.8
Ga = 69.9	43.5	In = 113.4	90.3	Tl = 203.7
-----	-----	Sn = 117.4	89.0	Pb = 206.4
As = 74.9	47.1	Sb = 122.0	88.0	Bi = 210.0
-----	45.1	Sb = 120.0	87.5	Bi = 207.5

"In the case of osmium, however, its atomic weight appears to be some six or seven units too large, whilst that of indium appears about two units too small. No conclusion can be drawn as to whether the atomic weight of antimony is 120, as found by Schneider and confirmed by Cooke, or whether it is 122, as found by Dexter and confirmed by Kessler.

"Although the difference between the atomic weight of arsenic and antimony is 47 when the number 122 is accepted, yet the latest determinations of Cooke show that the number 120 is to be preferred.

"It may, however, be safely asserted that should Schneider's number prove to be correct, his determination of the atomic weight of bismuth, viz. Bi = 207.5, is probably correct, whilst Dexter's atomic weight of antimony is only adapted to Dumas' atomic weight of bismuth, viz. Bi = 210."

But these comparisons deal with units rather than with tenths and hundredths. Meyer continues:

"The relations of the differences between the atomic weights justify us in making a selection from different experimental results; still our knowledge is too uncertain to allow of theoretical adjustments of numbers obtained by experiments. There can be no doubt that these differences are subject to law."

Mendeleyeff, in his Faraday lecture (*Jour. Chem. Soc.*, 55., 641) says :

"In the theory of numbers only do we find problems analogous to ours, and two attempts at expressing the atomic weights of the elements by algebraic formulæ seem to be deserving of attention, although neither of them can be considered a complete theory, nor as promising finally to solve the problem of the Periodic Law. The attempt of E. J. Mills (1886) does not even aspire to attain this end. He considers that all atomic weights can be expressed by a logarithmic function,

$$15 (n - 0.9375^t)$$

in which the variables  $n$  and  $t$  are *whole numbers*."

By this formula the atomic weights of the first 10 elements differ from the calculated values by a little less, and the next 20 elements by a little more than numbers selected at random.

Another logarithmic formula is that of Dr. G. J. Stoney. An abstract of his paper published in the *Chemical News* (57., 163, 1888), and in other periodicals, says that in plotting the atomic weights as ordinates of a diagram, the effort to extract information from the resulting curves was a failure. In plotting their cube roots, however, he found two logarithmic curves with perturbations, which showed distinct laws of increase for perissads and artiads. That for the perissads is expressed as follows :

$$Ym = k \log \left[ a \left( m + \frac{1}{2} \sin \frac{m\pi}{27} + \frac{1}{2} \sin \frac{m\pi}{18} + \text{subsequent terms} \right) \right]$$

the next being probably either  $-\frac{1}{2} \sin \frac{m\pi}{9}$ , or  $-\frac{1}{2} \sin \frac{m\pi}{9}$ .

This is a much more complicated expression than Cooke's original formula ( $a + nd$ ) which appears to be far more significant in its bearing upon the question of the structure of atoms.

Moreover with all the perturbations, the calculated values do not appear to coincide with the observed values as closely as those of the Perissad Law.

An "Approximate Algebraic expression of the Periodic Law of the Chemical Elements," by Prof. Carnelly, was published in

the Philosophical Magazine as recently as January, 1890. Prof. Carnelly says: "In 1885 I proposed for the chemical elements the general formula.

$$A_n B_{2n} + (2 - x)$$

in which  $n$  is the series and  $x$  the group to which the element belongs;  $A=12$  and  $B=-2$ .

"Since that time, and for the thirteen years previously, I have made frequent attempts to find a simple numerical expression for the Periodic Law, but so far without marked success. Early in the past summer, however, I obtained an expression, which, though only approximate, may still be found of considerable interest." This expression takes the form

$$(6.6 m + \sqrt{v})$$

in which  $m$  denotes the series and  $v$  the number of the group of Mendeleyeff's classification.

The deviations from his calculated values range from 0.1 to 6.7. Their mean value is 1.9, and 33 out of 54 are greater than unity.

The Rev. Dr. Haughton has perhaps done as much as any one to call attention to this important problem of representing the relation of atomic weights by algebraic expressions, and his well known geometric illustrations cannot fail to be both interesting and instructive to students of chemistry and mathematics.

Dr. Haughton calls attention to the constant increase of the artiad series from C to Si by locating them upon the same straight line in his diagram, which also shows the break in the series between O and Mg where his straight line crosses the axis.

#### RESULTS OF COMPARISON.

Referring to column (7) Table 1 showing the group in the Mendeleyeff series to which the element belongs and bearing in mind that Groups I., III., V. and VII. of this series correspond to the perissads and II., IV., VI. and VIII. to the artiaids, it appears that all of the first series of regular increase are perissads except Co and Zn, and all of the second series are artiaids except Sc and Cu of these, Cu and Zn are connecting links between the first and second groups.

Co perhaps belongs to another series, and Sc is little known.



The first groups of the first and second series have the common difference of 4.01 and 4.00 respectively. Their first terms are 7.04 and 12.09. Hence it follows that the difference between any term of the first series and the next term of the second should be about a unit. This is true for seven couples, and only fails where a term is missing from one of the series. In the same manner the difference between any term in the third group of the second series and the next term of the first series should be about one and a half units. Nothing can be predicted about the relation between the second groups owing to the irregularity of the second series in that group.

Comparing the second series column (5) Table 1 with the last of atomic weights in column (2) we find no element corresponding to the terms 20.09, 36.09, 83.30 and 131.16, nor is it probable that an element will be discovered with an atomic weight corresponding to these numbers, for the reason that they occur at that place in the series where the change from electro-negative to electro-positive occurs.

No element corresponds with 63.30, but the second group of the second series to which this term belongs is so irregular that it would be unsafe to base any prediction upon the common difference assumed for this series. More accurate determinations of some of the atomic weights of this group are much to be desired.

If praseodymium maintains its claim to a place in the series with an atomic weight of 143.6, it corresponds with the term 143.5 better than cerium.

The determination  $\text{Sc}=44.08$  brings it in the second series with the artiads, although it is regarded as a triad. It is not impossible that subsequent determinations may find a value nearer to 43.10, its calculated place in the first series. If philippium has a place in the series it should lie between 45 and 48\* and perhaps correspond to 47.10, leaving 44 or 43 for some other element. If it can be demonstrated that any other atomic weight than that of scandium lies between 40 and 48, the law of the octaves will have to be stated in broader terms than heretofore.

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\*Crooke's Researches on the Rare Earths, *Chem. News*, 60, 28.

The Perissad law would thus hold true if two more elements were inserted in the fourth series of Mendeleyeff than are provided for therein.

Whether the eighth group of Mendeleyeff should be associated with that group of common differences which precedes or with that which follows it, remains to be determined. It is also uncertain whether terms will ever be found between the several groups of constant increase near the atomic weights, 60 and 100.

The position of tellurium in the series has always been unsatisfactory. The old value was about 128, which is greater than that of iodine, whereas analogy would make it less.

Brauner has worked hard to find the true value. He is not yet satisfied with his results, and asks his brother chemists to leave the problem to be worked out by him. (*Jour. Chem. Soc.*, 55, 411—July, 1889.)

He says: "According to the recent determinations made by J. P. Cooke as well as those of Stas, these elements have the following atomic weights, Sb=119.96 and I=126.86, and we may therefore expect that the atomic weight of tellurium will be still smaller than 125, namely, about 123.5."

This is only another illustration of the fact that the Periodic law furnishes no guide whatever to determine the exact value of atomic weights. The Perissad law would give the following value for tellurium, viz.:  $124.87 + .11 = 124.98$ . This value depends, however, upon that of the other six elements in the third group of the second series, which are not as well known as those of the first groups.

#### INFERENCES.

The deviations from regular increase cannot be expected to correspond in every case with the chemical and physical properties, and in the present state of knowledge it would be impossible to form any conclusion from such comparisons, which, nevertheless, are valuable in the way of suggestion.

Table II. shows that in groups I. and VII. of the Mendeleyeff classification, the atomic weights found by observation are on an average in excess of those obtained by calculation.

In a general way the elements whose deviations are positive are chemically active, readily fusible, strongly electro-positive or electro-negative, and have the greatest atomic volumes. On the other hand those whose deviations are negative, are chemically and electrically neutral, are fusible only with great difficulty, and have small atomic volumes.

The general bearing of the Perissad Law upon the structure of atoms cannot be stated in better terms than those of Dr. Cooke, quoted at the beginning of this paper, viz.: "that the atoms of the members of the same series are formed of a common nucleus, to which has been added one or more groups of atoms, or perhaps one or more single atoms to which the corresponding element has not been discovered."

The law has been suggested to the writer of this paper as follows:

A mathematical analysis of molecular forces shows that if gravitation is the controlling force at minute as well as at sensible distances, then it must follow that the particles of which an atom is composed are to a great extent arranged in lines and not scattered promiscuously nor homogeneously through the space occupied by the atom. In other words matter must be fibrous or reticular, having a skeleton or frame work which holds together the mass, which is perhaps surrounded by an atmosphere of ether. This supposition is not so improbable as to be dismissed without due investigation. If the skeleton is composed of particles in rapid motion, in orbits nearly rectilinear, and if the surrounding ether is of a discontinuous nature and also in rapid motion, these motions are sufficient to counterbalance the tendency to collapse due to the force of attraction.

Whether this or any other of the assumptions about the constitution of matter be true, both the Perissad and the Periodic Law have an important bearing upon the problem.

Whatever opinion may be held with regard to the genesis of chemical atoms there can be no question that the masses vary according to some law.

Perhaps, for instance, an atom of aluminium has been formed by the addition to an atom of sodium of one or more other particles having a weight of four, perhaps by addition to one of magnesium

of a weight of three, or to one of boron of a weight of sixteen; perhaps on the other hand an atom of sodium has been formed by the loss of a weight of four from one of aluminum, etc. In all these cases the structure may be regarded as the same, and the phenomena may be investigated by treating a heavier atom as composed of a lighter one with something added to it. The above supposition, however, is at variance with that which assumes that the several atoms are composed of essentially different substances. The question of the constitution of matter is one of vital importance to the science of chemistry and can only be solved by a systematic course of investigations. On this point Victor Meyer in his address at Heidelberg, Sept. 18 1889, says:

“Has it not been in our own day that the most prominent orator amongst German naturalists, one who astonishes us by the comprehensiveness of his knowledge, has adopted as his own Kant's judgment on chemistry, namely, that ‘chemistry is a science, but not a science in the highest sense of the word, that is, a knowledge of nature, reduced to mathematical mechanics.’ \* \* \*

“If, without question, it is the aim of all natural science to understand phenomena so fully that they may be described in a mathematical form and, as far as they are unknown, may be predicted, a science which is so far distant from this aim as to look merely for the *path* that shall some day lead to it, must be considered as in its infancy. In the present stage our way of thinking and acting has this peculiarity. \* \* \* Before we can arrive at a mathematico-physical treatment of chemical phenomena in general, two fundamental problems must be solved; an hypothesis which allows a control by experiment (even within the same limits which to this day are imposed upon physics in regard to the law of gravitation), must answer these questions:—*What is Chemical Affinity?* and *what is Valency?*”

Two paths are presented and each should be pursued until it leads to an improbable conclusion, or furnishes a further clue to the solution of the problem.

The first path above mentioned appears far more promising, and the bearing of the Periodic and Perissad Laws upon this problem can be explained by a general illustration as follows:

## PLATE II.

4 8	Li.	4 8 4	B.	4 8 4	F.
4 4 4	Na.	4 4 4	Al.	4 4 4	Cl.
1 1 1	Li.	1 1 1	B.	1 1 1	F.
1 1 1	Na.	1 1 1	Al.	1 1 1	Cl.

O

$$\begin{array}{ccc} 3 & 1 & 3 \\ & 4 & 1 \\ 3 & 1 & 3 \end{array}$$

F

$$\begin{array}{|c|c|c|} \hline 3 & 1 & 3 \\ \hline 1 & 4 & 1 \\ \hline 3 & 1 & 3 \\ \hline \end{array}$$

\*

S

$$\begin{array}{ccc} 3 & 1 & 3 \\ \begin{array}{|c|c|c|} \hline 3 & 1 & 3 \\ \hline 1 & 4 & 1 \\ \hline 3 & 1 & 3 \\ \hline \end{array} & 1 & \\ 3 & 1 & 3 \end{array}$$

Cl

$$\begin{array}{|c|c|c|} \hline 3 & 1 & 3 \\ \hline \begin{array}{|c|c|c|} \hline 3 & 1 & 3 \\ \hline 1 & 4 & 1 \\ \hline 3 & 1 & 3 \\ \hline \end{array} & & \\ \hline 3 & 1 & 3 \\ \hline \end{array}$$

\*

Cr

$$\begin{array}{ccc} 3 & 1 & 3 & 1 \\ \begin{array}{|c|c|c|} \hline 3 & 1 & 3 \\ \hline 3 & 1 & 3 \\ \hline 1 & 1 & 4 & 1 & 1 \\ \hline 3 & 1 & 3 \\ \hline 3 & 1 & 3 \\ \hline \end{array} & 3 & \\ 3 & 1 & 3 \end{array}$$

Mn

$$\begin{array}{ccc} 3 & 1 & 3 & 1 \\ 1 & \begin{array}{|c|c|c|} \hline 3 & 1 & 3 \\ \hline 3 & 1 & 3 \\ \hline 1 & 1 & 4 & 1 & 1 \\ \hline 3 & 1 & 3 \\ \hline 3 & 1 & 3 \\ \hline \end{array} & 3 \\ 3 & 1 & 3 \end{array}$$

Fe

S

$$\begin{array}{ccc} + & + & + \\ 3 & 1 & 3 \\ - & \begin{array}{|c|c|c|} \hline 3 & 1 & 3 \\ \hline 1 & 4 & 1 \\ \hline 3 & 1 & 3 \\ \hline \end{array} & 1 + \\ 3 & 1 & 3 \\ + & + & + \end{array}$$

Cl

$$\begin{array}{|c|c|c|} \hline 3 & 1 & 3 \\ \hline \begin{array}{|c|c|c|} \hline 3 & 1 & 3 \\ \hline 1 & 4 & 1 \\ \hline 3 & 1 & 3 \\ \hline \end{array} & & \\ \hline 3 & 1 & 3 \\ \hline \end{array}$$

\*



Suppose the atom to be composed of a framework with an envelope of ether, and represent the structure upon a plane surface simply for the convenience of illustration.

According to one interpretation of the Perissad Law the atoms of the first group of the first series have been formed from a nucleus of 3 by the addition to it 1, 2, 4, 5, 6, 7, 8, 9, 12, 13 and 14 times of particles having a weight of about 4, and the other groups and series in similar manner.

These increments may have been added to all the extremities up to a certain point and then they may have formed around other points of the atom, or the whole increment may have united to one extremity, the next to another, etc., as shown in Plate II. In the case of elements whose deviations are additive, the excess over the regular increase may be referred to the greater amount of ether associated with the corresponding atoms.

By another interpretation of the Perissad Law of regular increase an artiad atom may have been formed by the addition of 1 to a perissad, then a perissad by the addition of 3 to an artiad, etc., as shown in Plate III. These diagrams suggest answers to the questions, *What is Chemical Affinity, what is Valency?*

Remsen (Theoretical Chem., 1887, p. 287) says of Chemical Affinity :

“ We know that when hydrogen and chlorine are brought together they combine with a great evolution of heat. \* \* \* The phenomenon suggests such phenomena of attraction as those of gravitation, electricity and magnetism. We, therefore, picture to ourselves the atoms of hydrogen and chlorine as drawn together by an attractive force, much as the stone thrown upwards is drawn to the earth or as the electrified body is attracted by other bodies. In each case to separate the attracted substances an expenditure of energy is necessary. Without any conception in regard to the nature of this chemical force we may for convenience call it *chemical affinity*. The first object in view in the study of this force is to measure its intensity in different cases. What is the difference between the attraction exerted between hydrogen and chlorine and that exerted by hydrogen and oxygen, etc., etc.? Is it dependent upon the nature of the substance, or is it independent of the nature and only dependent on the mass? ”



If the path upon which we have set out proves to be the correct one, it will probably lead to the conclusion that the attractive force is not only similar to but identical with gravitation. The arrangement of the particles in lines increases the intensity more than enough to make up for the small masses as compared with the masses of sensible objects. Atomic repulsion is caused by the kinetic energy or centrifugal force of ether, of which the atoms are composed, and with which they are surrounded; but when they are brought together by external pressure upon the masses or by a loss of heat and diminution of the repulsive forces, the skeletons come within the spheres of their mutual attractions and the union takes place. If the ether is more condensed around the lines forming the skeleton and if it revolves around these lines as axes, the chemical and electrical conduct of the atom may depend upon what part of the skeleton projects so far as to influence the neighboring atoms.

Valency may be described as follows: If we refer the repulsive force produced by the motion of the ether to equipotential surfaces, we may say that a monad atom has one point projecting beyond one of these surfaces, a dyad atom two points, etc. The difference between an electro-positive and electro-negative atom may depend upon the direction in which the ether revolves as suggested by the theory of Ampère or by the fact that one atom exposes a re-entrant to another's salient, as suggested by Table III. Dr. Asche also refers to this combination in a paper on Didymium, read before the British Association in 1889. In the last line of Table III. the electro-positive and negative bonds are expressed by + and — respectively. Much is known and much remains to be known about the position of these bonds in space. The diagram on a plane surface is so generally employed in chemistry that no misapprehension can arise from this form of illustration.

## CALCULATION OF BLAST FURNACE SLAGS AS PRACTISED IN CERTAIN WORKS IN EUROPE.

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By AUGUSTE J. ROSSI, C. E.

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In another paper (this journal, Vol. 12, 6, 7) we have described a practical method of calculating the charges of a blast furnace in order to obtain a slag of a given type, which does not require the use of any formula or chemical symbol. It may be interesting to compare it with the method followed in certain works, in Eastern France, to arrive at the same result.

What is called "a charge" is this certain weight of ore, limestone and fuel, in relative proportion to each other, which are charged in a furnace at regular intervals of time during twenty-four hours. Technically, it is more properly the calculated weights of the relative qualities of limestone and ore necessary to obtain a given composition of slag, the quantity of fuel per ton of iron smelted, or per charge, being, as a rule, a factor which is assumed and which practice has taught, but subject to ulterior corrections as may be required.

The coal is supplied to furnish, by its combustion, the heat and the elements necessary for the chemical reactions which take place and only its ash contributes to the ultimate composition of the slag. In France, the charge is called "*lit de fusion*," an expression, it seems to us, having a more appropriate meaning than the vague term "charge." The total amount of ore and stone constitutes "*a lit de fusion*," "a charge," with an assumed quantity of fuel and the proportion of the two materials, ore and stone, are the elements to be calculated, bearing in mind the character of the slag desired as indicative of a special grade of pig iron and the percentage of ash of the fuel and its composition.

## CALCULATION OF A SLAG AT THE WORKS X.

The formula of the slag expected was that of a "Seisgulo-Silicate" (monosilicate of Percy),  $3\text{RO}, \text{SiO}_3$  or  $2\text{RO}, \text{SiO}_2$  (orthosilicate, bibasic slag); oxygen of acid=oxygen of base.

Two different kinds of ore were used, of which the composition is given below, the calculations being based on the determination of the *free* oxygen in the materials, demand a certain technical knowledge.

## 1.—Gangue of Ore A.

$\text{SiO}_3$	8.50	Equiv. $\text{SiO}_3$	=45.3	Oxygen of $\text{SiO}_3$	= $8.50 \times \frac{24}{45.3}$	=4.50
$\text{Al}_2\text{O}_3$	5.50	"	$\text{Al}_2\text{O}_3$	=51.5	"	$\text{Al}_2\text{O}_3$ = $5.50 \times \frac{24}{51.5}$ = 2.56
$\text{CaO}$	5.00	"	$\text{CaO}$	=28	"	$\text{CaO}$ = $5.00 \times \frac{8}{28}$ = 1.43
$\text{MgO}$	0.90	"	$\text{MgO}$	=20	"	$\text{MgO}$ = $0.90 \times \frac{8}{20}$ = 0.31

## 2.—Gangue of Ore B.

SiO <sub>3</sub>	29.55	} on an average { it was taken to be	SiO <sub>3</sub> ; 25.00..O of Acid	SiO <sub>3</sub>	13.24
CaO	0.15		Al <sub>2</sub> O <sub>3</sub> ; 3.50..O of Base	Al <sub>2</sub> O <sub>3</sub>	1.63
Al <sub>2</sub> O <sub>3</sub>	3.40				
Free oxygen, acid.....					11.61

## 3.—Ash of Coal.

SiO <sub>3</sub> =47.80	O of SiO <sub>3</sub> -----	25.32
Al <sub>2</sub> O <sub>3</sub> =33.00	“ Al <sub>2</sub> O <sub>3</sub> -----	15.37
CaO = 6.00	“ CaO -----	1.71
MgO = 3.20	“ MgO -----	1.28
	Free oxygen, acid -----	6.96

## 4.—Limestone.

SiO <sub>3</sub>	= 2.50	O of SiO <sub>3</sub>	=-----	1.32
Al <sub>2</sub> O <sub>3</sub>	= 2.00	“ Al <sub>2</sub> O <sub>3</sub>	=-----	1.10
CaO	=52.50	“ CaO	=-----	15.00
				16.10
Free oxygen, basic-----				14.78

## Resume.

Free O, acid, in ore A	0.20
" " " B	11.61
" " in ash of Coke	6.96
" O, basic, in limestone	14.78

Assume 360 kilos. of good coke at 10% of ash, a quantity judged sufficient for "a charge" or "*lit de fusion*," taken to be = 880 kilos. stone and ore. This gives 36 kilos. of ash corresponding to

$$36 \times \frac{6.96}{100} = 2.50 \text{ free oxygen of acid in the ash.}$$

Let  $m$  be the weight of ore A to be used, in kilogrammes.

"  $f$  " " " B " "  
"  $c$  " " of limestone " "

Then: The total free oxygen acid =  $0.20 m + 11.61 f + 2.50$ .

Total free oxygen, basic =  $14.78 c$ , and since we want to obtain a bibasic slag, that is one in which oxygen, acid = oxygen, basic.

$0.20 m + 11.61 f + 2.50 = 14.78 c$ , but we have also the equation of condition, total charge:  $\underbrace{f + m}_{\text{Ore.}} + \underbrace{c}_{\text{Stone.}} = 880$ ; we have then

two equations containing three unknown quantities. Eliminating  $c$  between the two we come to the final equation:

$14.98 m + 26.39 f = 13003.90$ , an equation which is indeterminate, as it should be, since the proportions of ore A and ore B, within the above limits, are evidently optional. Assuming for  $m$  certain values we find:

$m = 50$	$f = 464.50$	$c = 365.50$
$m = 100$	$f = 436.00$	$c = 344.00$
$m = 200$	$f = 379.25$	$c = 300.75$
$m = 300$	$f = 322.45$	$c = 257.55$

and the charges will be:

Ore A..... 50.	} 514.50 kilos. }	Or such others based on the other values of $m$ , $f$ , $c$ . Coke always = 360 kilos.
Ore B..... 464.50		
Limestone..... 365.50		
Coke..... 360.00		

The ores had about 35% metallic iron, hence 514.50 kilos. of ore would yield  $514.50 \times 0.35 = 180$ , iron, and taking the first solution, the relative proportions of the different materials in one charge for one of iron must be:

Ore.....	2.85	} for $m = 50$ .
Stone.....	2.03	
Coke.....	2.00	

Adopting the first solution let us calculate the composition of the slag and verify its bibasic character.

	Ore A = 50 Kgs.	Ore B = 464.50.	Coke = $\left( \begin{smallmatrix} \text{Ash} \\ 10\% \end{smallmatrix} \right) 36.00 \text{ Kgs.}$	Stone = 365.50.	Totals in Slag.
Silica .....	$\frac{8.50}{100} \times 50 = 24.5$	$\frac{25.00}{100} \times 464.50 = 116.12$	$\frac{49.80}{100} \times 36 = 17.90$	$\frac{2.50}{100} \times 365.50 = 9.13$	146.70 Kgs.
Alumina .....	$\frac{5.50}{100} \times 50 = 2.75$	$\frac{3.50}{100} \times 464.50 = 16.26$	$\frac{33.00}{100} \times 36 = 11.88$	$\frac{2.00}{100} \times 365.50 = 7.31$	38.90 "
Lime .....	$\frac{5.00}{100} \times 50 = 2.5$	.....	$\frac{6.00}{100} \times 36 = 2.16$	$\frac{53.50}{100} \times 365.50 = 191.89$	196.55 "
Magnesia .....	$\frac{0.90}{100} \times 50 = 0.45$	.....	$\frac{3.30}{100} \times 36 = 1.15$	.....	1.60 "
Totals .....	9.95	132.38	33.39	306.33	383.05

Reducing to lime :

$$\begin{array}{rcl}
 \text{Silica} & = & 146.70 \\
 \text{Al}_2\text{O}_3 & = & 38.20 \times 1.631 = 62.27 \text{ CaO} \\
 \text{CaO} & = & 196.55 \\
 \text{MgO} & = & 1.60 \times 1.40 = 2.24 \\
 & & \hline
 & & 407.76
 \end{array}$$

Reducing to a percentage, we find :

$$\begin{array}{rcl}
 \text{SiO}_2 & = & 35.90 \\
 \text{CaO} & = & 64.10 \\
 \hline
 & & 100.00
 \end{array}$$

The type, exactly bibasic, has the composition

$$\left\{ \begin{array}{l} \text{SiO}_2 = 34.88 \\ \text{CaO} = 65.12 \end{array} \right.$$

The slag is practically a bibasic slag, as closely as possible using two decimals or only one, as in the analyses.

Let us calculate this same slag by the method of reduction to *lime*, adopting the same data and two indeterminate quantities of the ores A and B.

*Ore A:*

SiO <sub>2</sub> .....	=8.50.....	8.50
Al <sub>2</sub> O <sub>3</sub> .....	=5.50 × 1.63 = 8.95	} CaO 15.21
CaO.....	=5.00 × 1. = 5.00	
MgO.....	=0.90 × 1.49 = 1.26	

The saturation for a bibasic slag is 0.538 SiO<sub>2</sub> for 1 lime. 15.21 lime will take then: 15.21 × 0.53 = 8.18 SiO<sub>2</sub>, leaving 0.32 to 0.33% free silica to be saturated for 1 of ore.

*Ore B:*

SiO <sub>2</sub> .....	=25.00.....	25.00
Al <sub>2</sub> O <sub>3</sub> .....	= 3.50 × 1.63 ..	2.71 CaO

571 CaO will saturate 3.07 SiO<sub>2</sub>, leaving 21.93% free silica for 1 of ore.

*Ash of Coke (10% × 360 = 36 Kilos.)*

SiO <sub>2</sub> .....	=47.80.....	47.80
Al <sub>2</sub> O <sub>3</sub> .....	=33. × 1.63 + = 53.79	} 64.27 CaO
CaO.....	= 6.....	
MgO.....	= 3.20 × 1.40 = 4.48	

64.27 CaO will saturate 64.27 × 0.538 = 34.58 silica, leaving in ash

13.22  
13.22% free silica. For 36 ash  $\frac{13.22}{100} \times 36 = 4.76$  free silica.

*Stone:*

Silica.....	=2.50.....	2.50
Al <sub>2</sub> O <sub>3</sub> .....	=2.00 × 1.63 + 3.26	} 55.76
CaO.....	=.....	

1 silica takes up 1.858 lime to make a basic slag. Hence: 2.50 silica will take 2.50 × 1.858 lime = 4.65 lime, leaving as free lime in the stone 51.11%.

Let  $m$  be the amount of ore A taken as before,  $f$  that of ore B,  $c$  that of stone. We have then:

Free Silica in Ore A .....  $m \times 0.33$   
 " " in ash of Coal .....  $c \times 4.76$   
 " " in Ore B .....  $f \times 21.93$

Total free *silica* in ores and coal:  $0.33 m + 21.93 f + 4.76$

Total free *lime* in stone:  $51.11 c$

and since the free lime of the stone must saturate the free silica of the ores, stone and ash, at the rate of 0.538 silica for 1 of lime the 51.11  $c$  of free lime in stone will take up  $51.11 \times 0.538 c = 27.50 c$  of *silica*. We have then this equation free silica to saturate  $0.33 m + 21.93 f + 4.76 = 27.50 c$  silica saturated by stone. All the terms

being expressed in *silica*,  $\text{SiO}_2$ , if we multiply them *all* by  $\frac{8}{15}$ , which

does not change the equation, we shall have the relation of equality of the oxygen found previously by the other method as near as the difference of the numbers expressing the equivalents of silica formerly, and now (taking only one or two places of decimals) we have the differences appearing only in hundredths as already observed.  $0.18 m + 11.68 f + 2.15 = 14.66 c$ , instead of  $0.20 m + 11.61 f + 2.50 = 14.78 c$ . We have a second equation of condition the same as in the first method:  $f + m + c = 880$ . By combining these two equations and taking  $m = 50, 100$ , etc., we shall find the same figures as already calculated or differing only in hundredths.

# THE AERATION AND COMPOSITION OF NIAGARA RIVER WATER ABOVE AND BELOW NIAGARA FALLS.

BY DR. ALBERT R. LEEDS.

The great height of Niagara Falls and the churning up of its waters at the base with the large volumes of air mechanically carried down into the deep basin below the Falls appeared to afford a good opportunity of examining into the question of the aeration so produced, and the chemical changes, if any, resultant therefrom.

With these objects in view, and with the assistance of Dr. F. P. Vandenberg, the City Chemist of Buffalo, I collected duplicate samples of the water both below and above the Falls. The former were taken on the American side at a point, so near the Falls that we were well wet with the spray during the short interval required to secure the samples; the latter were collected at the upper end of Goat Island. The collection was made July 9th, 1890.

The dissolved gases were as follows :

IN ONE LITRE: VOLUMES STATED IN CUBIC CENTIMETERS.						
Above the Falls.			Below the Falls.			
	(1)	(2)	Mean.	(1)	(2)	Mean.
Carbon Dioxide	0.96	0.79	0.875	0.89	0.84	0.865
Oxygen .....	4.93	5.22	5.075	5.02	5.29	5.155
Nitrogen .....	11.94	13.00	12.47	12.12	13.05	12.58
Total Gases.....	17.83	19.01	18.42	18.03	19.18	18.605

On making a comparison of the mean results, it would appear that the sum total of the air in the water collected below the Falls is 0.185 cubic centimetre per liter greater than in the water above; the oxygen is 0.08 c. c. more, and the nitrogen is 0.11 c. c.



450 AERATION AND COMPOSITION OF NIAGARA RIVER WATER.

greater. The ratio of the dissolved nitrogen to the dissolved oxygen in both sets of samples is nearly 72.3 to 27.7 This is a low ratio for the oxygen, and is to be considered in relation to the character of the Niagara River water, which has a yellow color, due to a considerable amount of peaty extractive matter.

The three constituents which it was thought might have experienced sufficient change as to admit of the detection of the alteration by chemical analysis were the ammonia, the albuminoid ammonia and the organic matter as measured by the oxygen required to effect its oxidation. The results were as follows :

IN PARTS PER 100,000.						
Above the Falls.				Below the Falls.		
	(1)	(2)	Mean.	(1)	(2)	Mean.
Ammonia.....	Lost.	0.0056	----	0.0058	0.006	0.0 59
Albuminoid ammonia.	0.0114	0.0106	0.011	0.0108	0.011	0.0109
Required oxygen.....	----	0.226	----	----	0.226	----

It would not answer to draw any inferences from these figures as to a change of composition due to the contact with a slight increase of dissolved oxygen during three or four seconds' interval. Samples taken below the Whirlpool, which is some distance below the Falls, might exhibit quite a different result.

## COMPOSITION OF SWILL MILK.

BY DR. ALBERT R. LEEDS.

The Dairy Commissioner of the State of New Jersey, under the impression that the milk supplied by cattle entirely stall-fed upon the swill and brewery grain obtained from New York hotels and breweries would afford milk of quality below the State standard, and objectionable or dangerous on other accounts, has recently submitted a sample of this milk to me for examination. The cattle were in dark, dirty and ill ventilated stables, the principal alleviation of their condition being that afforded by a great abundance of excellent spring water for drinking. At the time of collecting the sample, which represents the milk of a number of cows, the animals appeared to be all in good physical condition.

The milk was normal in color, smell and taste, with slightly acid reaction. Its specific gravity at 15° C. was 1.0309.

Instead of giving very low percentages, all its constituents were as high in amount as is usual in the milk obtained at the same season of the year (November) from dairy cattle. The composition was :

Albuminoids .....	3.469	per cent.
Fats .....	5.17	“ “
Lactose .....	4.427	“ “
Ash .....	0.749	“ “
Total .....	13.815	

A plate culture of from one drop, one-twentieth of a cubic centimeter, showed the presence of 4,200 colonies of bacteria after the lapse of eighteen hours, with so numerous a proportion of liquefying colonies that further counting was discontinued.

The swill fed to these cattle was accompanied by a large amount of brewers' grains, the latter indeed being the chief component of the food. There was no hay, or other feed, nor were they at any time put on pasturage.

## A NOTE ON ALUM PHOSPHATE BAKING POWDERS.

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BY LUCIUS PITKIN, PH. B.

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The point of view from which healthfulness or unhealthfulness has been predicated for the combinations usually employed as leavening agents has been shifted considerably during the last few years. The main contention has been, and continues to be, in regard to the advisability of alumina compounds in such food products, but the positions assumed by both advocates and opponents have been not only modified, but on some points reversed.

It will be conceded, we think, that much of adverse opinion in regard to the employment of burnt alum in baking powders has arisen from confusion concerning two very distinct purposes for which alum has been used.

Its peculiar action upon flour producing a whiter and lighter bread from inferior and in some cases unsalable flour than could otherwise be obtained, early led to its adoption in England and on the Continent, for the purpose of enhancing the value of bread products beyond their legitimate value. It was thus a fraud upon the consumer, calling for and being met by legislative restriction; nor should it be forgotten that the alum was added to the bread as crystallized alum possessing, when in the bread, all the properties of that salt, and being extracted therefrom in large proportion by water.

In the use of alum in baking powder the conditions are entirely changed; the powder being used by the buyer, the purpose for which legislative interference was first invoked is no longer a factor and from a sanitary point of view the question is no longer

centered on alum as such, but on hydrate and phosphate of alumina.

In the celebrated Norfolk baking powder case (*Analyst* 4, page 231) it was contended that the phosphate of alumina was entirely insoluble in the human system, that thus the flour was deprived of its phosphatic constituents by the alumina in the powder forming insoluble residues, and on that account alum baking powders should be condemned. With the advent of acid phosphate of lime as used in combination with burnt alum for liberating the carbonic acid of sodium bicarbonate such objections were forestalled, since much more phosphoric acid was introduced than could possibly be removed from the flour.

The reversal of opinion to which we alluded was now taking place and statements and calculations made were based upon the assumption that all of the alumina left in the residues of bread and biscuit was taken up in the system, whereas it had been claimed before that they were insoluble.

Direct experimentation made on a typical phosphate and alum composition seemed, however, to be at variance with such assumptions since in the nearest approach possible to the actual conditions the factor arrived at for the solubility of residues from phosphate and alum powders in the mouth and stomach was found to be  $\frac{1}{4}$  to  $\frac{1}{5}$  of the alumina present (*Pitkin, Journal American Chem. Soc.* 9, p. 27).

The consideration of the effect of the residues from the various powders upon digestion now began to be taken up, and much attention was bestowed upon that aspect of the question in the various State Boards of Health and Government reports. Some comparative figures on the action of the various combinations have been published (*Pitkin, Journal Am. Chemical Soc.*, Vol. 12, 8) which seem to indicate that, in albuminoid digestion at least, there is little difference between the action of residues from cream of tartar and alum phosphate powders, while sour milk and soda also seems to exercise an almost identical inhibitory action. The basis upon which these results were obtained was a comparison of residues from neutralization of the same quantities of sodium bicarbonate—in other words, equal leavening equivalents of the residues were employed.

In glancing over a late Government Report (Food and Food Adulterants, Part 5th, Bulletin No. 13, p. 575) we find the following table :

Powders.	Carbonic Acid Gas. Per cent.	Total residue of the weight of Chemicals used. Per cent.
Tartrate.....	16.	104
Phosphate.....	22.	123
Alum.....	27.	128
Alum and Phosphate.	17.	111

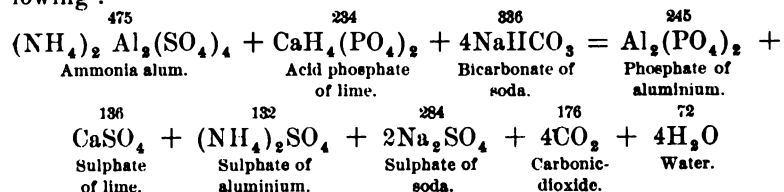
As will be seen at a glance the alum and the phosphate powders give the least residue per unit of gas evolved, while the alum and phosphate combination is credited with the greatest percentage of residue to carbonic acid. When it is remembered that it is upon the amount as well as upon the character of residues that attention is now specially directed, it is obvious that the ratio is a matter of no little importance.

One would naturally suppose that such a combination powder would be somewhat intermediate in its leavening action between the two classes to which it is related.

Looking over the report to see upon what data the figures quoted were obtained we find, p. 571 :

“A case in which the character of the powder appears to be improved by such mixing, however, is furnished by the alum and phosphate powders.

This combination seems to be a favorite one with manufacturers. In fact there are now comparatively few “straight” alum powders in the market, most of the cheaper grades being made of mixtures in various proportions of the alum with acid phosphate of lime, the reaction it is intended to obtain is probably the following :



On page 567 in discussing phosphate powders, 234 parts of  $\text{CaH}_2(\text{PO}_4)_2$  is credited with the power of liberating 88 parts of carbon dioxide: on page 569, 475 parts of  $(\text{NH}_4)_2\text{Al}_2(\text{SO}_4)_4$  liberates 264 parts of carbon dioxide, but by the equation used in discussing alum phosphate powders only half enough sodium bicarbonate is given to the above quantities of "acid phosphate" and burnt alum to liberate the 88+264 parts of carbon dioxide which they would separately set free.

We think the published analyses in the report conclusively prove that while the combination may be "a favorite one with manufacturers," they certainly do not intend to obtain the reaction with which they are credited. No such ratio is found to exist between the ingredients in a single one of the fifteen complete analyses of alum phosphate powders printed in the bulletin.

All baking powders lose more or less carbonic acid on keeping, depending upon the amount of moisture absorbed, quantity of "filler" present, length of time elapsing since manufacture, etc. It will therefore be advisable to examine the ratios between, for instance, the sulphuric anhydride and sodium oxide (both being proportionally increased by any loss in carbonic acid gas) called for by the formula and that found in actual analysis.

By the formula  $(\text{SO}_3)_4$  corresponds to 4 Na or 2  $\text{Na}_2\text{O}$  by weight 320 parts of sulphuric anhydride should be found for each 124 parts of sodium oxide or the ratio of  $\text{SO}_3$  to  $\text{Na}_2\text{O}$  should be more than 2.5 to 1.

In the analyses we find:

No. 5510.....	$\text{SO}_3 = 9.79\%$	$\text{Na}_2\text{O} = 12.25\%$
" 5511.....	" = 11.02%	" = 12.58%
" 5512.....	" = 11.57%	" = 14.04%
" 5515.....	" = 13.01%	" = 9.83%
" 5516.....	" = 12.26%	" = 9.21%
" 5517.....	" = 13.18%	" = 8.33%
" 5519.....	" = 8.78%	" = 7.26%
" 5520.....	" = 10.51%	" = 11.92%
" 5521.....	" = 11.54%	" = 11.20%
" 5524.....	" = 10.14%	" = 10.87%
" 5525.....	" = 8.93%	" = 12.15%

No. 5530.....	" = 10.57%	Na <sub>2</sub> O = 10.32%
" 5532.....	" = 11.30%	" = 11.36%
" 5533.....	" = 10.66%	" = 12.69%
" 5534.....	" = 13.23%	" = 12.29%

By averaging the above it will be seen that the percentages of sodium oxide and sulphuric anhydride are practically equal, instead of corresponding to the ratio demanded by the formula, nor is ratio of phosphoric acid to sodium oxide much closer to what is demanded. There is evidently a mistaken assumption therefore upon which the high ratio of residue to leavening power has been asserted of this class of powders, and the influence attaching to such an exhaustive report from such a source forms a sufficient excuse, I trust, for calling attention to the error.

## NOTES UPON WATER ANALYSES BY THE AMMONIA METHOD WITH SOME NEW APPARATUS.\*

BY A. A. BRENNEMAN.

Wanklyn's ammonia method of water analysis, in spite of its imperfections, is still the process most widely used in this country. It is the simplest and most practicable of all combustion methods, wet or dry, that have been applied to water analysis, and although it shares with all processes of this class used in sanitary work, the doubt as to interpretation of its results, its general use among chemists indicates its superior adaptability to such work.

The process as now used is essentially the original one, but experience has shown that the interpretation of results must be guided by familiarity with the method and by a knowledge of the class to which the water in question belongs. Also, there is now a marked tendency to prescribe more closely than Wanklyn has done the minute details of the process.

The variability of natural water with respect to the indications which they yield under Wanklyn's process, as to time of distillation, concentration of reagents and rate of attack of oxidizable matter, have necessitated the adoption of standard methods as the nearest approach to a means by which the results obtained from different waters, and by different observers, could be made in any sense comparable.

I have shown in a previous paper (*This Journal*, Vol. 8, No. 9) the points in which such prescription of detail should be insisted upon and have suggested a standard method for general use. The previous work of Mallet, Smart, and others, had suggested many similar points of detail requiring attention.

The Report of the Committee of the Chemical Section of the American Association for the Advancement of Science for 1889

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\*Read at the Newport Meeting.



upon the methods of water analysis adopts many of these different suggestions. With regard to the quantity of water to be used the quantity is left optional, as to 500 or 100 c.c., in this report. In common with many other chemists I should have been glad to see a recommendation as to the exclusive use of the 100 c.c. method and of 10 c.c. nesslerizing tubes as representing a neater and more accurate method of conducting the analysis. The use of the smaller quantity of water is no exception to the general preference in chemical analysis for small samples where accuracy is not impaired by their use. In the present case there are to be offered the advantages of less cumbrous apparatus, a hastening of the process and an increase in accuracy by the use of the smaller tubes with their greater depth for a given volume of the liquid submitted to the colorimetric test.

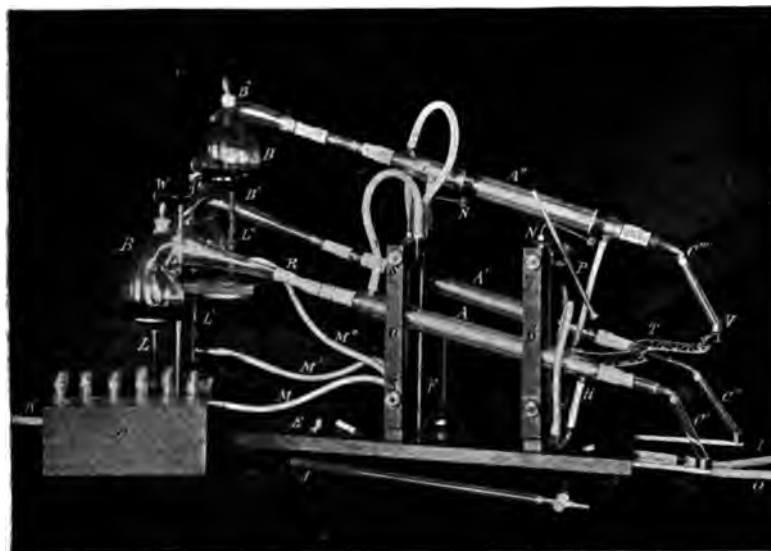
Another detail upon which I have insisted, as necessary in order to render results obtained by the Wanklyn process comparable, as nearly as possible, for waters of all classes, is the matter of carrying the distillation to a very small residual volume in the retort, so that the greatest strength of the permanganate and alkali and the strongest attack upon oxidable matter shall be concentrated upon the organic matter which has longest resisted that attack; in other words the carrying of the distillation to a point near dryness. This again is much more easily done in a small than in a large retort, for obvious reasons. Further, the accurate measurement of all liquids put into the retort permits a control of the distillation by measurement of the 10 c.c. portions which are taken off as distillates during the operation, or of the 85 c.c. portion taken off in the preliminary process of cleansing the retort as already described. (*loc. cit.*) The degree of condensation may thus be judged of and the volume of the residual liquid in the retort at the close of the operation may be known within 2-3 c.c. at most. In practice I leave less than 5 c.c. of liquid in the retort at the close, yet accidents from running dry or spurting are almost unknown.

The objection that modification of the old method will prevent comparison of the results with those previously obtained, is an objection that, in some sense, meets every attempt at improvement of an analytical process and cannot be regarded as insuperable.

In the present case, the difference under the prescribed conditions is not such as to cause confusion, while the gain in comparability of all results obtained by the modified method among themselves, as compared with the same comparability under the old method, is of the greatest importance.

In connection with the foregoing I present a holder for retorts and condensers which has been used in its present form for water analysis during about four years and has been found very convenient.

It permits simultaneous examination of three samples of water, while the entire apparatus in operation can be lifted or moved without injury to any of its parts. The latter consideration relates to the prevention of accidents which sometimes occur from slight movements of pieces of glass apparatus rigidly connected but resting upon different bases, and its advantage will be readily understood. The management of these retorts and their distillates is just sufficient to keep one person steadily occupied; with one or even two retorts there is much waiting time with the consequent temptation to neglect the apparatus temporarily for other work.



The cut will be readily understood.

The condensers are held between cork-faced jaws D, D', by clamp screws S, S'. Water for cooling enters by the rubber tube I and escapes through O. Gas enters by K. and is distributed by a tube forked above the base to connect with the rubber tubes M, M', M''. The water tubes H and F are similarly forked above the base. The nessler tubes C', C'' rest in sockets which slide, by square brass rods, into deep holes in the base through a brass plate on the edge of the base, and are very steady and smooth in motion. The japanned bracket supporting C''' swings sidewise but can be fixed by a single motion, rigidly in the position shown. The upper retort B'' can be lifted off, with its condenser, as it rests only in vertical holes upon the shanks of the clamps N, N'; the inclination of the condenser, however, is controlled by two small set-screw collars on the shanks.

As auxiliary apparatus we may mention the tube block, C, having tapering holes, wide at the top and made of wood first stained and then saturated throughout with paraffin which is, lastly, well rubbed in. It is very firm and convenient for rapid handling of the nessler tubes.

The stirring pipette, P, has a beaded end and a short, wide tip below the bead. It is held in an ordinary spiral pen rack fastened to the stand. The caps E, of rubber tube and glass rod are used to close the condenser tubes when not in use; much time is thereby saved in freeing the retort from ammonia. The burette J, graduated to 0.5 c.c. is used for measuring nessler solution of which 0.5 c.c. is used for each 10 c.c. of distillate.

## SYNTHESES IN THE SUGAR GROUP.

BY EMIL FISCHER.

(Concluded.) *from paper 40*

Translated by L. H. FRIEDBURG, Ph. D.

Analysis and synthesis meet at this point, since i-mannite is identical with synthetical  $\alpha$ -acrose, and it was an easy matter to prove that  $\alpha$ -acrose, regenerated from the osazone is nothing else than i. fructose.<sup>1</sup> In order to conclude the synthesis of natural sugars it remains only to search for the transition of the middle inactive series into the side series.

The fundamental work of *Pasteur* taught us two methods for the transformation of inactive substances into optically active ones: partial fermentation by bacilli, or splitting by crystallization of the salts. With sugars, only the first way is applicable. Here, yeast is to be preferred to mold ferments and splitting ferments as used by *Pasteur* and others. An aqueous solution of synthetical  $\alpha$ -acrose ferments actively in a short time with beer yeast. In one to two days the fermentation is completed. The liquid, previously inactive, then rotates strongly to the right and furnishes a d-glucosazone, since the yeast left behind in it the *laevo-fructose*.<sup>2</sup> It may seem surprising, that a sugar of strongly dextro-rotary power is enumerated here as a laevo compound. But the signs d. and l. are not intended to express in every case the power of rotation, which changes without regularity, but rather the *chemical* nexus of these compounds. The letter d. has been chosen for the group of natural sugars because most of them turn towards the right. But in consequence it has also to be maintained for fruit sugar, which, in spite of its power of rotation to the left, belongs to the same geometrical series as the d-mannose.

<sup>1</sup>*Ber. d. chem. Ges.*, **23**, 384 and 387.

<sup>2</sup>*Ber. d. chem. Ges.*, **23**, 389.

The action of beer yeast upon i-mannose is quite analogous, the dextro part ferments and l-mannose remains behind.<sup>3</sup>

In both cases the yeast uses up that part of the inactive substance to which it clings by force of past evolution.

But this method only leads to the less interesting sugars of the l series. In order to obtain the natural products of the d series synthetically, chemical methods are required, which lead on to the end by the following reactions.<sup>4</sup>

Careful oxidation of i-mannite with nitric acid furnishes i-mannose which by means of bromine water is transformed into i-mannonic acid. This latter is split by means of the strychnia—morphia—salt into d- and l-mannonic acids, from which result by reduction, the optically active mannoses and mannites. Then the way leads from d-mannose and its glucosazone to d-fructose.

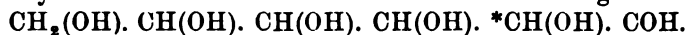
In the mannite series there remains now only the synthesis of glucose and its derivatives and isomeres, which have been enumerated in the glucose group of the table above. We mentioned that glucose is stereo-isomeric with mannose. [The older assumption of glucose as the aldehyde of mannite was proved to be erroneous by the discovery of mannose. But I have furthermore convinced myself of this fact by a new research of the reduction of grape sugar by sodium amalgam. Working in the old way, allowing the sugar solution to remain over the amalgam, the operation lasts for weeks and then really furnishes mannite, however in a quantity proportionally small. But if the detrimental action of the alkali is prevented by frequent neutralization with sulphuric acid, and if by continuous agitation the action of the amalgam is accelerated, the reaction is accomplished as swiftly as with mannose and other aldehydic sugars. Using quantities of 10 grms., twelve to fifteen hours finish it; no mannite is then obtained, at least its quantity is so trifling that I was unable to isolate it. Instead, a syrup results which is easily soluble in alcohol and which most likely contains a hexatomic alcohol, stereo-isomeric with mannite. (Compare also, C. Scheibler, *Ber. d. chem. Ges.*, **16**, 3010.)]

Glucose and mannose both furnish an identical glucosazone and

<sup>3</sup>*Ber. d. chem. Ges.*, **23**, 382.

<sup>4</sup>*Ber. d. chem. Ges.*, **23**, 389.

consequently the isomery between the two depends upon asymmetry of that \*carbon atom marked \* in the following formula :



Thus it might be expected that a reciprocal transformation of the two compounds was feasible. These easily decomposed sugars, however, do not admit of the experiment. The pertaining acids do, however, by heating them with quinoline.\*

I chose this tertiary basis because it cannot form amido-like compounds, and because it is so easy to remove it again from the mixture of reaction.

Gluconic acid heated with quinoline to 140°C. is partly transformed into mannonic acid ; conversely this latter, under similar conditions, yields a considerable quantity of gluconic acid. These observations recall the known reciprocal conversion of racemic acid and mesotartaric acid.

Now, since gluconic acid is transformed by nascent hydrogen into glucose, the total synthesis of this latter is realized.

Exactly the same process leads from l-mannonic acid to the compounds optically isomeric with gluconic acid and grape sugar. They are enumerated in the above table as l-gluconic acid and l-glucose. The preparation of l-gluconic acid from l-mannonic acid by heating with quinoline signifies its synthesis, but this procedure is so circumstantial and yields so little that the acid would perhaps not have been found, unless it had been met with and studied on another path. Curious to say this l-gluconic acid forms abundantly from arabinose by aggregation of hydrocyanic acid. Along with it is formed arabinose carboacid, isolated by Kiliani. The simultaneous formation of two stereoisomeric products on addition of hydrocyanic acid to aldehydes, which here was observed for the first time, is very remarkable, theoretically as well as practically. According to expectation l-gluconic acid is deceptively similar to the d-compound and both acids unite in aqueous solution to a third inactive substance which forms independent salts as well as other inactive derivatives.

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\*Ber. d. chem. Ges., 22, 374.

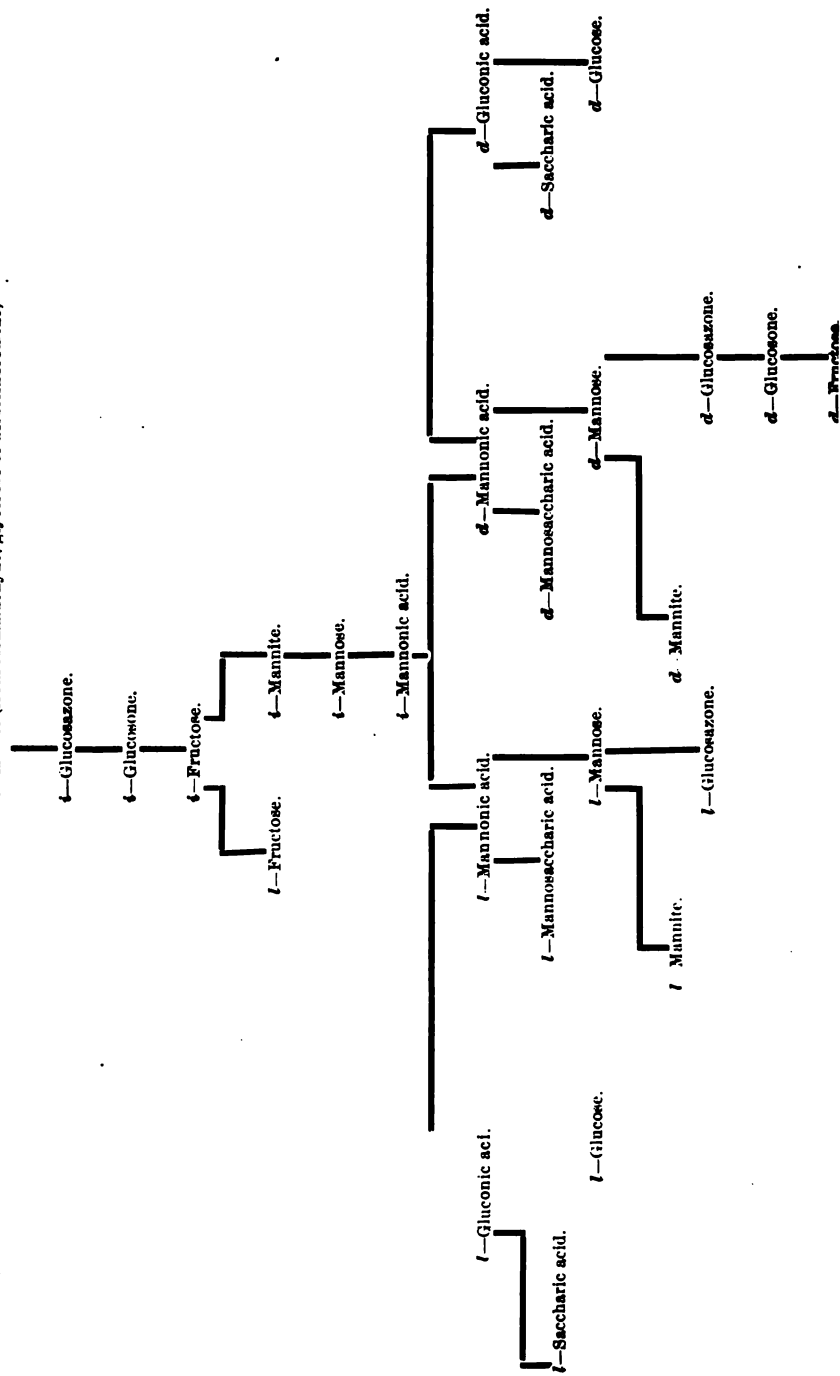
\*Ber. d. chem. Ges., 23, 799.

From l- and i-gluconic acids we obtain by reduction the optical isomeres of glucose (enumerated in the above table as l- and i-glucose) ; by oxidation l- and i-saccharic acids are formed.

Leaving the nitrogenized products aside, we now know no less than 26 bodies of the mannite series which may be subdivided into the fructose, mannose and glucose groups:

One might feel tempted to use this rich material as a touchstone for the consequences of Le Bel-van't Hoff theory. Let it suffice to say that all compounds fit into the general frame of this theory, but that, most likely, our views in regard to the union of isomeric substances with asymmetric carbon atoms has to be modified.

All members of the mannite series are joined by transitions, all of them are to be obtained by direct synthesis. The following table gives a systematic view of this latter, beginning with  $\alpha$ -acrose.

[illegible]



Thus we are now enabled, starting from one of the simplest of carbon compounds, formaldehyde, to prepare the two most important natural sugars.

But upon the basis thus gained the synthesis leads further on to sugars containing a greater number of carbon atoms. Any one of the previously mentioned "oses" can be transformed into an acid, richer in one carbon atom, by aggregation of hydrocyanic acid. The lactone of any such acid, when treated with sodium amalgam, will be reduced to a corresponding sugar, and starting from this latter, the modus of building up a higher compound can be repeated in a similar manner.

In this way Passmore and myself have obtained from mannose a compound  $C_9H_{18}O_9$ , and thus far we are unable to see the limit of this mode of procedure.

The older nomenclature is not sufficing for the denotation of these numerous synthetical products. I have therefore proposed a new one<sup>1</sup>, which temporarily meets the want.

The sugar is named according to the number of carbon atoms which it contains: Triose, tetrose, pentose, hexose, heptose, octose, nonose and the different isomeric products receive a prefix, indicating their derivation. This nomenclature seems to collide with<sup>2</sup> Scheibler's proposal to call sugars:  $C_{1,2}H_{2,2}O_{1,1}$  (the so called saccharoses) bioses, and sugars:  $C_{1,3}H_{3,2}O_{1,1}$  trioses. In reality the two proposals are easily combined in forming the words, hexobiose and hexotriose. For the general distinction of aldehyde and ketone sugars, Armstrong's names, aldose and ketose, seem well fitted.

The greatest hindrance to suitable names for the now known optically isomeric sugars is offered by the words heretofore in use, laevulose and dextrose. It will be good to drop them altogether in spite of the famous authorship of Berthelot and Kekulé. Instead of dextrose, the old name glucose may be used, and for laevulose I have used above the non-ambiguous name fructose, to which Liebermann drew my attention.

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<sup>1</sup>*Ber. d. chem. Ges.*, 23, 934.

<sup>2</sup>*Ber. d. chem. Ges.*, 18, 646.

The preferences of the new nomenclature are very obvious in the following table, which contains all now known simple sugars :

Trioses : Glycerose (mixture of glycerolaldehyde and dioxyacetone).

Tetroses : Erythrose (most likely a mixture of aldose and ketose).

Pentoses : Arabinose (aldose).

Xylose.

Methylpentose : Rhamnose (aldose).

Hexoses : d-l-i. Glucose } (aldoses) } Mannite series.  
               d-l-i. Mannose }  
               d-l-i. Fructose (ketose) }

Galactose (aldose of dulcete series).

Sorbinose.

Formose } (unknown constitution).  
 $\beta$ -acrose }

Methylhexose : Rhamnohexose (aldose).

Heptoses : Mannoheptose,	}	(aldoses).
Glucoheptose,		
Galaheptose,		
Fructoheptose,		
Methylheptose : Rhamnoheptose		
Octoses : Mannoctose,	}	
Glucoctose,		
Nonoses : Mannononose,		

Glycerose and erythrose have been explicitly dealt with before. Amongst the pentoses we find arabinose and xylose<sup>9</sup>. The first is an aldehyde with normal carbon chain, and belongs to the l- mannose series. The constitution of the second is not yet determined. Rhamnose must be considered as a methylpentose with normal carbon chain.

The number of hexoses we find considerably increased. Grape sugar and fruit sugar are to be seen here as d- glucose and d- fructose ; along with them we find their optical isomers.

Galactose and sorbinose stand as isolated as formerly. Formose and  $\beta$ -acrose are too scantily investigated as to judge about their constitution. It appears unlikely that they should contain a normal carbon chain.

<sup>9</sup> Wheeler and Tollen's *Ann. Chem. Pharm.*, 254, 304.

Rhamnohexose (methylhexose) has been prepared synthetically from rhamnose by aggregation of hydrocyanic acid. The same is true for the following heptoses, octoses and nonoses, the origin of which is expressed by the prefixes. Most of these products surpass in their capacity of crystallization, and in beauty the derivatives of natural hexoses.

The most interesting of them is the mannnononose, *because it ferments with beer yeast as easily as glucose*. This property is wanting to the octoses, heptoses and pentoses, but we find it existing with most hexoses and with glycerose. Yeast, therefore, seems to incline to the number three and its multiples.

In comparing this table with the one first given, which represented the sugar group of a few years ago (Journ. Am. Chem. Soc., 12, 340), we recognize the extent of the newly gained territory.

Many of these artificial sugars will certainly be found some day in plants. Indications exist, since the heptatomic alcohol, which is generated from mannoheptose by reduction is identical with *perseit*, occurring in the fruits of *Laurus Persea*, which, according to newer researches of Maquenne<sup>10</sup> has the formula  $C_7H_{16}O_7$ . But these observations are only of secondary importance; they are a mere by-products of the new methods. The centre of interest is offered by the synthesis of grape sugar and fruit sugar, since it is suited to open the understanding of one of the grandest and most remarkable physiological processes, that of formation of carbohydrates in the green plant. As far as our knowledge reaches, grape and fruit sugar are the first products of assimilation, and they thus form the carbon-bearing material from which the plant prepares all other organic compounds. Up to this day practically nothing is known about the process of natural formation of sugar. All attempts of explanation are mere hypotheses, the value of which may be disputed. If in spite of this, I shall now mention one, this is only done in order to point out the path on which, perhaps, the results of my researches may be utilized for physiological experiments.

According to the view of Baeyer, carbon dioxide is reduced at first within green leaves to formaldehyde. This latter, then,

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<sup>10</sup> *Compt. Rend.*, 107, 583; and *Ann. Chim. Phys.* [6], 19, 1.

by condensation is transformed into sugar. Since heretofore it has not been possible to prove the existence of quantities of formaldehyde notable in some degree in leaves, it may perhaps be more proper to search for other intermediate products, particularly for glycerose, according to the now known methods.

And even of more interest seems this other question : chemical synthesis leads, as we have seen above, starting from formaldehyde, in the first place to optically *inactive* acrose. In contrast to this we have found in plants heretofore exclusively the *active* sugars of the d-mannite series. Are these the only products of assimilation? Is it a prerogative of the living organism to prepare optically active substances. Is here a particular cause active, a sort of vital force? I do not believe it, but incline towards the view that it is merely the imperfection of our knowledge which surrounds this process with the halo of a miracle.

Not one known fact exists, to directly deny that the plant at first prepares *inactive* sugars, just as chemical synthesis does, that then it splits these using the members of the d-mannite series to build up starch, cellulose, inuline, etc., etc., while the optical isomers serve other purposes, still unknown to us.

This question will soon be answered by a closer study of the sugars occurring in plants, since the methods given facilitate this work greatly.

These considerations have brought us to the territory of limits between chemistry and physiology and thus I will touch another problem, the experimental treatment of which lies nearer to the biologist than to the chemist.

The natural carbohydrates next to the albuminoids are the most important food for the animal, particularly for herbivora, and we possess a great number of valuable observations in regard to the fate of these in the body of the animal.

May it not be possible to replace these natural carbohydrates entirely or partly by some of the artificial sugars and what then would be the consequence?

Mannose, standing so near to grape sugar and so easily fermentable by yeast, will be most likely, even for the higher organized animal a food ; and still this small change of material may cause corresponding changes in physiological processes.

After partaking of mannose will a new glycogen be produced by the liver, will a substitute for milk sugar be formed by the mammary gland, will the system of the diabetic be able to oxidize this sugar?

In offering as a food to the animal body a pentose, heptose or even the easily fermentable nonose, the physiological changes would become still more visible. We would find that the blood and the tissues were modified in their functions, the pig or the goose would produce another fat, the bee another wax.

This experiment should even be carried further.

The assimilating plant builds up from sugar not only the more complicated carbohydrates and the fats, but also with the auxiliary inorganic nitrogen compounds, the albuminoids. The mold and splitting organisms do this likewise.

Now, in nourishing the assimilating plant or those organisms by means of a differently composed sugar, they might be forced to even produce a different albumen. And then should we not expect that the change in building material would have as a consequence a change of architecture? Thus a chemical influence upon the formation of an organism would be gained, which would lead to most peculiar phenomena: to changes of form which would leave behind them everything heretofore attained by breeding and cross breeding.

Since the fundamental work done by Wöhler and Frerichs<sup>11</sup> hundreds of organic compounds have been incorporated into the animal body, in order to trace (often in the most tedious manner) their products of decomposition in the urine. But physiological chemists have used almost exclusively material of not the slightest similarity with natural food.

A wide field of work is opened to them in the use of these new sugars, the results of such work promises, by far, more remarkable results.

Biology stands here before a question which, as far as I know, was never put before and could not very well be put, since chemistry had not furnished the material for the experiment.

The question is worthy of the experimental test.

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<sup>11</sup>*Ann. Chem. (Liebig)*, **65**, 335.

For the chemist proper enough work remains to be done with the carbohydrates. The mannite group, it is true, is completely built up as few other chapters of organic chemistry are, but in the dulcite series the old state of affairs prevails.

Supposing this group should in the very nearest time be opened as perfectly as its isomeric group, we would, nevertheless, know only eight hexoses of the structure of grape sugar, not counting the inactive compounds which allow of splitting.

But modern theory anticipates no less than sixteen, and it is very likely, according to experience in the mannite series, that they are all able to exist.

It is even not too much to foretell that the preparation, according to the methods described, will not be over difficult, as soon as it is possible to transform the different tartaric acids into the optically isomeric trioxybutyric acids.

A problem of a different nature is put to synthesis by the example of the plant, which, starting from hexoses, produces in an apparently simple manner the more complicated carbohydrates. The beginning has already been made by the preparation of diglucose and of artificial dextrines; thus the chemical synthesis of starch, cellulose, inuline, gum, etc., is only a question of time.

It seems to me that organic synthesis which, thanks to the splendid methods which we inherited from the old masters, has, within the short period of sixty-two years, furnished: urea, the fats, many acids, bases and colors of the vegetable class, finally uric acid and sugars, need not shrink before any product of the living organism.

## ABSTRACTS.

### GENERAL CHEMISTRY.

#### **Note on the Diamond.** ALBERT KRAUSE.

The proof that diamond and carbon are identical has not heretofore been strictly defined. It has been shown only that the atomic weight is the same, and that on combustion a gas is furnished which precipitates baryta or lime water. Consequently it has not been shown to be impossible that diamond and carbon may be similar to each other, as nickel is to cobalt. An exact determination of the carbon dioxide formed in each case should decide the question. A derivative of carbon dioxide, obtained from diamond and from carbon, was tested in regard to such constants as melting point, solubility, form of crystals and power of conducting electricity.

As a result it was found that sodium carbonate prepared from diamond is absolutely identical with ordinary sodium carbonate. (*Ber. d. chem. Ges.*, **23**, 2409.) L. H. F.

#### **On Vanadium Sulpho Salts.** KRÜSS and K. OHNMAIS.

Indications of the existence of vanadium sulpho salts existed previously. A series of beautifully crystallizing salts of this kind have now been prepared. (*Ber. d. chem. Ges.*, **23**, 2547.)

L. H. F.

#### **Researches on Beryllium.** KRÜSS and MORAHT.

As a result of these researches the atomic weight of Be was found to be 9.028 if O = 15.96; or if O = 16 then Be = 9.05. (*Ber. d. chem. Ges.*, **23**, 2552.) L. H. F.

#### **The Constitution of some double salts of Rhodium.** K. SEUBERT and K. KOBÉ.

The following salts were prepared and analyzed: rhodium-potassium-chloride; rhodium sulphite with sodium sulphite,

rhodium sulphate with sodium sulphate. This last mentioned salt must be considered an anhydrous rhodium-alum of the formula:  $\text{Rh}_2(\text{SO}_4)_3, \text{Na}_2\text{SO}_4$ . (*Ber. d. chem. Ges.*, 23, 2556.) L. H. F.

**Splitting of Ammonium Nitrite by Means of Platinum Sponge.** O. LOEW.

The facility of decomposition of ammonium nitrite, in aqueous solution (by warming) into nitrogen and water, decreases on increasing dilution. The more dilute the solution, the higher is the temperature required for decomposition, and thus very dilute solutions may be concentrated on the water bath to a certain degree without decomposition.

The author finds that, while a 4 to 5 per cent. solution, even on boiling is only slowly decomposed, this decomposition takes place at ordinary temperature in the presence of spongy platinum.

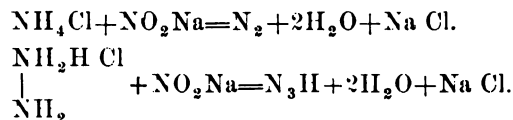
In a former paper it had been shown, that nitrogen in presence of strong alkalies and spongy platinum, reacts with water. Here we see the reverse action; free bases being absent, platinum sponge causes the liberation of nitrogen with formation of water. (*Ber. d. chem. Ges.*, 24, 3018.) L. H. F.

**On Hydrazoic Acid (Azoimide).** TH. CURTIUS.

Hydrazoic acid,  $\text{N}_3\text{H}$ , a surprising analogue to halogen hydrides, is formed under certain conditions by the action of nitrous acid upon diamide, water being split off. It has the constitution:



It is to be expected that just as ammonia and nitrous acid furnish nitrogen, hydrazinmonochloride and nitrites would yield azoimide:



However, it seems to be difficult to prepare azoimide in this direct manner. On the other hand the study of reactions between



hydrazinhydrate and benzoylglycolic acid ester or hippuric acid ester lead to the discovery of this well characterized, easily prepared and interesting compound of nitrogen and hydrogen.

Organic derivatives of azoimide have long been known. Griess discovered the diazobenzolimide and E. Fischer prepared it from nitrosophenylhydrazin, this latter being the phenylester of hydrazoic acid.

Azoimide is a gas of a very remarkable, pungent odor. Even in a state of dilution it creates dizziness and headache, with inflammation of the mucous membrane of the nose. Its aqueous solution painfully cauterizes the epidermis.

Azoimide is a strong, monobasic acid, comparable in every respect to hydrochloric acid. Hence it may be called hydrazoic acid (Stickstoff-Wasserstoffsäure).

The gas is easily absorbed by water. On distilling this aqueous solution, a very concentrated aqueous acid passes over between 90° and 100° C. The first distillates of this contained about 27 per cent. hydrazoic acid. The aqueous solution, if not too dilute, has the odor of the gas. Blue litmus paper is colored intensely red when held above the liquid. Ammonia gas produces dense fumes of ammonium azide. A seven per cent. aqueous solution of hydrazoic acid dissolves iron, zinc, copper, aluminium, and magnesium, hydrogen being liberated violently. It seems that the concentrated acid also attacks gold and silver, since it turns red when in contact with both these metals.

The nitrogen metals (azides) thus formed, comparable are in every way to the metallic chlorides.

The metals of silver nitrate and mercurous nitrate are precipitated, even from dilute solutions, quantitatively as  $N_3$  Ag and  $(N_3)_2 Hg_2$ . These reactions are used for the separation and purification of hydrazoic acid. Dilute sulphuric acid decomposes the solutions of all nitrogen metals, setting free the acid.

Silver azide was more closely studied. It differs from silver chloride only by its prominence under the influence of light.

Hydrazoic acid differs from halogen hydrides merely by its strong explosive properties which necessitate great precaution in handling it. The detonation caused by a few milligrammes of

silver azide or mercurous azide when heated or struck is unparalleled. A mere accident prevented the author being hurt when trying to enclose 2 c. c. of a 27 per cent. aqueous solution of azoimide in a specimen tube. The attempt to close the capillary end by fusion resulted in strong detonation reducing the thick glass vessel to powder. The sharpness of the sound, when a mere dust particle of silver azide is heated, is only comparable to the discharge of a Leyden jar.

The author is now beginning the study of reducing agents upon a nitrosamine which he obtained from hippuric acid. If it should be feasible (contrary to all observations heretofore made on nitroso compounds) to reduce the oxygen of the nitroso group, then it will be possible to split the amidohydrazin compound obtained into hippuric acid and triamide:  $\text{NH}_2 \cdot \text{NH} \cdot \text{NH}_2$ , by boiling with acids. This triamide would be the "propane" of the hydronitrogen compounds. This body might again be condensed to substances richer in nitrogen. Introduction of nitroso groups into these, allowing a reduction to amido groups, would lead to a new chemistry of nitrogen compounds analogous to the chemistry of hydrocarbons of alcohol radicles. (*Ber. d. chem. Ges.*, **23**, 3023.)  
L. H. F.

#### Preparation of Dry Diazo-Salts. E. KNOEVENAGEL.

Avoid water, replacing it by alcohol. Instead of working with a current of free nitrous acid, use amyl nitrite in acid solution for diazotizing.—(*Ber. d. chem. Ges.*, **23**, 2994.)  
L. H. F.

#### Formation of Urea from Albumen. E. DRECHSEL.

It was found by Lossen that on oxydizing albumen with alkaline permanganate solution, no urea, but small quantities of guanidine were formed. The author, studying the products of decomposition of caseine found two new bases, lysatine and lysatinine, isomeric with creatine and creatinine. From these new bases he obtained urea by further treatment with baryta water.

His researches are of importance, since they show that urea is formed from albumen, simply by hydrolysis and without any oxidation.

Lysatine has subsequently also been formed from glue, and conglutine. (*Ber. d. chem. Ges.*, **23**, 3096.)  
L. H. F.

**A new Photographic Process.** A. G. GREEN, C. F. CROSS and E. I. BEVAN.

The diazo compounds of dihydrothiotoluidine and its condensed derivatives when combined with the substance of animal or vegetable tissue are highly sensitive to light. A cotton or silk tissue dyed with primuline (1 to 2 per cent.) and sensitized by diazotizing of this latter, represents a photographic plate, able to yield a perfect "positive" in 40 to 180 seconds exposure. Thus a perfect reproduction of the original, in the shape of diazoprimuline, takes place. This picture then may be "developed" in form of any of the different colors which are formed from the above by combination with amines or phenoles. (*Ber. d. chem. Ges.*, **23**, 3131.)

L. H. F.

**On Fucose, from sea weed (Fucus), an isomer of Rhamnose.** A. GÜNTHER and B. TOLLENS.

This crystallizable sugar from sea weed was obtained by the hydrazone reaction. It is very soluble, of sweet taste, crystallizes slowly, like laevulose, forms distinctly microscopic needles and plates, and has the identical composition of rhamnose:  $C_6H_{12}O_6$ .

Fucose rotates strongly to the left and, in the beginning, shows multi-rotation. On distilling it with HCl drops of methyl furfural are formed. Alkaline copper solution is strongly reduced by fucose: (1 c. c. of Fehling's solution = 6 to 7 mgrms. fucose).

The melting point of its hydrazone is  $+170^{\circ}C$ .; that of the osazone, about  $159^{\circ}C$ . Fucose is therefore isomeric, but entirely different from rhamnose. (*Ber. d. chem. Ges.*, **23**, 2585.)

L. H. F.

**A Quantitative Determination of Antimony according to Marsh's Test.** A. VON BYLERT.

The author refers to the paper of Kuhn and Saeger (*Ber. d. chem. Ges.*, **23**, 1798), and points out that Gautier (*Bull. Soc. Chim.*, **2**, 250, 1875) founded a quantitative determination of arsenic upon Marsh's test.

In the determination of antimony, Marsh's method has been modified. Antimony was used in the form of alloys. These were dissolved in mercury and a liquid sodium amalgam, prepared by dis-

solving 5.5 grms. Na in 25 c. c. Hg, was added. Thus sodium-antimony is formed, which is decomposed by dilute sulphuric acid. Small quantities of antimony were thus determined in alloys of tin, silver, antimony.—(*Ber. d. chem. Ges.*, 23, 2968.) L. H. F.

**Experiments for quantitative determination of arsenic by Marsh's test. Behavior of arsine towards potassium hydrate.** B. KUHN and O. SAEGER.

An abstract of this paper is to be found in *Jour. Amer. Chem. Soc.*, 12, 353. In regard to the behavior of arsine towards potassium hydrate it must be stated that R. O. Doremus has drawn attention to this fact, as observed by him, long ago. See: Fresenius quantitative analysis. Allen and Johnson's Translation. John Wiley & Sons, New York, 1881, p. 782. L. H. F.

**Determination of Carbon in Organic Compounds, in the Wet Way.** J. MESSINGER.

In an apparatus of peculiar construction, made by Cornelius Heinz, in Aix-la-Chapelle (Aachen), the determination of carbon in organic compounds is performed by means of chromic acid and conc. sulphuric acid. (*Ber. d. chem. Ges.*, 23, 2756.) L. H. F.

**A Method for the Quantitative Determination of Camphor.** F. FOERSTER.

Substances occur in the trade consisting of nitrocellulose and camphor. Both substances are very intimately combined in these horn or ivory-like masses. Such substances are decomposed by means of sodium hydrate solution and subjected to distillation. Thus the camphor is driven off. The distillate is shaken with a measured quantity of benzol, and the rotation of the solution obtained is determined.—(*Ber. d. chem. Ges.*, 23, 2981.) L. H. F.

**Volumetric Determination of Phenols.** I. MESSINGER and G. VORTMANN.

In a former paper (*Ber. d. Chem. Ges.*, 22, 2312.) the authors have described a new class of bodies formed by the reaction of iodine upon an alkaline solution of phenols. This reaction has now been developed into a mode of quantitative determination (volumetrically) of phenol, thymol, naphthol and salicylic acid. (*Ber. d. chem. Ges.*, 23, 2753.) L. H. F.

## Abstracts of American Patents Relating to Chemistry.

(From the U. S. Patent Office Gazette.)

Issued November 18, 1890.

**440,639.**—Blue black azo dye. R. Lanch and M. Kahn.

Violet to blue black dye stuffs, consisting of diazotized tetrazo compounds or naphthols (dioxynaphthalines), said dye stuffs being soluble in hot water and insoluble in benzine and alcohol, and having the property of dyeing cotton without a mordant.

**440,752.**—Apparatus for preparing extract of coffee. H. Barotte.

**440,754.**—Art of manufacturing illuminating gas. E. Beauharnais.

**440,772.**—Preparing yeast. E. Leconte.

A method of revivifying and removing the bitterness from brewers' yeast to fit the same for bread making, which consists in diluting the yeast with warm water and adding maltine or extract of malt.

**440,777.**—Process of obtaining oxygen. F. Salomon.

Consists in heating a mixture of a metallic oxide, such as lead monoxide or lead carbonate, and of an alkaline earth, such as lime, in a current of air, so as to cause oxygen to be absorbed, and then driving off the oxygen by a current of carbon dioxide.

**440,792.**—Process of making hydrogen peroxide. W. Erwin.

**440,830.**—Process of treating coal tar. A. L. Munson.

The tar is heated to 110° F. and thoroughly combined with a solution of zinc chloride and oil of turpentine.

**440,921.**—Explosive. D. Mindeleff.

Consists ethyl nitrate, methyl nitrate, nitrobenzol, methyl alcohol, pyroxyline, and nitroglycerine.

**440,946.**—Welding compound. T. Durrant.

Consists of borax, brick or marble dust, potassium bicarbonate, and salts of tartar.

**440,950.**—Apparatus for manufacturing heating or fuel gas. A. Kitson.

**440,952.**—Manufacture of compound aluminium plates. C. H. Land.

**440,953.**—Blue dye. W. Majert.

The process of preparing consists in melting alphanaphthylidis ulpho acid with caustic soda or potash, then treating the dioxynaphthaline so obtained with concentrated or fuming sulphuric acid, or sulphuric chlorhydrin, and then adding the sulpho acid of dioxynaphthaline so obtained to tetrazodiphenyl chloride in presence of sodium carbonate.

**440,963.**—Apparatus for extracting grease from wool. L. Pinagel.

**440,968.**—Carbonizing apparatus. A. Silverberg and C. Detering.

**441,010.**—Leather dressing. J. M. Jolly.

Consists of neat's foot oil, water, beeswax, logwood extract, gum arabic, petrolatum, borax, oil of citronella and castile soap.

**441,075.**—Paint. J. Smith.

Consists of white lead, linseed oil, whiting, sulphate of lime, alum, glue, driers and water.

**441,076.**—Apparatus for producing white sugar. C. Steffen.

**441,102.**—Process of reducing iron ores. H. W. Last and J. Johnson.

Iron is reduced directly from the ore, by grinding the moistened ore and carbonaceous material together into a pulverized homogeneous mass, spreading the paste thus formed in the hearth of a furnace, covering the charge with a mixture of pulverized glass and carbon, and then subjecting the mass to heat to effect the reduction.

*Issued November 25, 1890.*

**441,163.**—Non-conducting sheet or mass. H. W. Johns.

Consists of fibrous or comminuted sponge, and horn blende, mineral wool, the oxides of the metals, and the like bodies, and antiseptic or disinfecting material.

**441,164.**—Fireproofing compound. H. W. Johns.

Consists of borax, boric acid and zinc oxide.

**441,165.**—Non-conducting covering. H. W. Johns.

Composed of a major part of wood pulp mixed with infusorial earth, magnesia or like material and with straw, sponge, or like porous of fibrous material and with a layer of fireproofing material between the covering and the surface to be protected.

**441,166.**—Process of reducing ore. J. Johnson.

Iron is reduced direct from the ore, by charging the ore onto the hearth of a suitable furnace, subjecting it to a reducing heat, adding dampened pulverized carbonaceous material to the charge and rabbling or stirring it into the hot ore, and then subjecting the entire charge to a reducing heat.

**441,174.**—Process of manufacturing carburized metal. H. W. Last and J. Johnson.

Ore and carbonaceous material are reduced to a homogeneous pasty mass, which with a carbonaceous fuel is charged into a cupola furnace.

**441,180.**—Making peptones. V. Marciano.

Finely chopped meat is subjected to the action of a vegetable ferment until peptonization takes place, after which the peptonized meat is dissolved in water and filtered.

**441,181.**—Making peptonized meat. V. Marciano.

The process consists in subjecting finely chopped meat to the action of the organic vegetable ferments contained in the juice expressed from the

plants belonging to the family of *Bromeliaceas* until peptonization takes place, then evaporating and drying the liquid peptonized meat, and grinding it into powder.

**441,182.**—Making vegetable pepsin. V. Marcano.

The juice from *Bromeliaceous* plants is evaporated at a temperature not exceeding 45° C to a density of 40° B and precipitated with alcohol.

**441,284.**—Chemical feeder for filters. B. H. Coffey.

**441,290.**—Anti-fouling paint. M. E. Dejonge.

Consists of zinc dust suspended in a vehicle of a solution of shellac and colophony in fusel oil.

**441,291.**—Anti-corrosive and anti-fouling compound. M. E. Dejonge.

Consists of colophony, paraffin oil, paraffin and zinc dust.

**441,292.**—Anti-fouling paint. M. E. Dejonge.

Consists of paraffin, zinc dust and agalite.

**441,366.**—Process of hardening resins. A. Kissel.

Colophony and like inferior resins are hardened by first melting the resin with an oxide to neutralize the free resinous acid normally existing in the resin, and forming a hardened resin; second, treating the hardened resin thus formed with a soluble chemical to convert resinous acid generated or liberated in melting the resin into a soluble salt; and, lastly, separating the soluble resinate from the hardened resin.

**441,462.**—Method of treating parchmented fibre waste. J. W. Barnes.

**441,501.**—Process of manufacturing rubber goods. G. C. Mandleberg, H. L. Rothband and S. L. Mandleberg.

**441,502.**—Process of manufacturing rubber goods. G. C. Mandleberg, H. L. Rothband and S. L. Mandleberg.

**441,503.**—Process of manufacturing rubber goods. G. C. Mandleberg, H. L. Rothband and S. L. Mandleberg.

**441,514.**—Manufacture of translucent enamel. J. Valère.

Consists of minium, boric acid, zinc oxide, stannic oxide, clean sand, soda, feldspar, fluor spar, potassium carbonate, calcium carbonate, borax sodium nitrate, and a suitable flux.

W. R.

## THE ANNUAL MEETING.

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The annual meeting of the society was held Friday evening, December 5th, 1890, in the University of the City of New York, Vice-President Breneman in the chair.

The minutes of the previous meeting were read and accepted. A letter was read from the retiring president, Dr. H. B. Nason. The Vice-President reported upon the state of the Society, and called attention to the increase in the membership, which had been over 30 per cent. in the past year. The treasurer's report, brought up to November 22d, was read by Treasurer King, and showed a similar improvement in the finances.

The Librarian reported that many books had been added to the library, and others bound, and that a list of the exchanges would be printed in the JOURNAL.

The report of the Committee on Papers and Publications, received through the Editor showed a marked improvement in the JOURNAL in every way, the yearly volume promising to be the largest ever issued.

The Committee on Conference which had been appointed in accordance with the resolution of the Newport meeting reported through Dr. Waller that Prof. Munroe had been obliged to resign. Prof. J. H. Appleton was appointed in his place. Dr. Waller thought it well to have the committee enlarged to five members. The matter was, on motion, placed in the power of the committee.

The Committee on Nominations reported through Dr. Doremus that it would be advisable to revise the By-Laws governing the admission of new members. It was voted to authorize the present committee on nominations to suggest the proper form of blanks and mode of procedure which it would be advisable to adopt.

The annual election was then held. Messrs. Geisler and Rupp were appointed tellers. The number of ballots cast was 61, resulting in the election of the officers for 1891, as follows :



## THE ANNUAL MEETING.

*President.*

GEO. F. BARKER.

*Vice-Presidents.*

- |                    |                 |
|--------------------|-----------------|
| 1. C. E. MUNROE,   | 4. ELWYN WALLER |
| 2. C. F. CHANDLER, | 5. EDWARD HART, |
| 3. A. A. BRENEMAN, | 6. F. A. GENTH. |

*Corresponding Secretary*, A. C. HALE.*Recording Secretary*, DURAND WOODMAN.*Treasurer*, F. T. KING.*Librarian*, WM. RUPP.*Curators.*

C. E. MUNSELL, J. CAWLEY, T. B. STILLMAN.

*Committee on Papers and Publications.*

A. A. BRENEMAN, J. F. GEISLER, WM. RUPP.

*Committee on Nominations.*

A. H. SABIN,	LUCIUS PITKIN,
A. P. HALLOCK,	C. A. DOREMUS,
J. B. MACKINTOSH.	

*Board of Directors.*

C. F. CHANDLER,	A. C. HALE,
A. A. BRENEMAN,	F. T. KING,
E. WALLER,	A. H. SABIN,
L. H. FRIEDBURG,	D. WOODMAN,
R. W. HALL,	A. P. HALLOCK,
W. MCMURTRIE,	J. F. GEISLER,
W. RUPP.	

*Advisory Council.*

For three years :

C. F. CHANDLER,	C. E. MUNROE,
T. G. WORMLEY,	J. H. APPLETON.

For two years :

A. A. BRENEMAN,	A. B. PRESCOTT,
F. A. GENTH,	J. W. MALLETT.

For one year :

T. STERRY HUNT,      H. B. NASON,  
S. W. JOHNSON,      G. C. CALDWELL.

The following gentlemen were unanimously elected to membership :

Jas. E. Talmage, Ph. D., J. A. Burns, Ph. D., S. G. Valentine, H. F. Carpenter, W. C. Ferguson, Ph.B., J. H. Washburn, Ph. D., Harry Mulliken, Dr. Edward P. Harris, H. S. Patterson, Nat. J. Lane, J. L. Perkins, J. A. Deghuae, J. J. Tobin, Harwood Huntingdon.

The following names were proposed :

ROBERT W. SCHEDLER, care of N. Y. Tartar Co., Ninth street and Gowanus Canal, Brooklyn.

J. W. BAIRD, Prof. Chemistry, Mass. Coll. Pharmacy, Boston, Mass.

JOHN B. LYNCH, M.D., Instructor in Histology, Coll. Phys. and Surg., N. Y.

L. MEYER CONNER, City Chemist, Dallas, Texas.

WM. D. PHILLIPS, 77 Pine st., N. Y.

JEROME W. FRANK, Standard Varnish Works, 734 E. 14th st., N. Y.

For Associate Membership, Mr. J. H. Saville, Thomasville, Ga.

The society was then adjourned to meet in Philadelphia, December 30 and 31.

CHAS. F. MCKENNA.

Recording Secretary.

## THE PHILADELPHIA MEETING.

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The second general meeting of the American Chemical Society was held at Philadelphia December 30 and 31 as announced.

Eighty chemists were registered at the meeting. The meeting was opened with a short informal address by Prof. H. B. Nason, President of the Society. Prof. G. F. Barker, President of the Society for 1891, presided at the second session, and delivered an inaugural address upon "The Borderland between Physics and Chemistry."\*

Twelve papers were read at the meeting. A conference of committees from different chemical organizations was held, and resolutions were adopted recommending the union of all American chemists in one body under the Constitution of the American Chemical Society, with such modifications as may be hereafter agreed upon. A further conference was recommended.

A full report of the Philadelphia meeting will appear in the January number of the *Journal*.

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\* This address will be printed in full in the January number.

## NOTES ON CERTAIN REACTIONS FOR TYROTOXICON.

BY H. A. WEBER, PH. D.

(*Prof. Agricult. Chem. Ohio State University, Columbus, O.*)

Through the Ohio State Board of Health and the Ohio State Dairy and Food Commission the writer has, within the last few years, received numerous samples of poisonous cheese for examination. The samples were tested for tyrotoxin according to the well known method as published by Dr. Vaughan. About 1,500 grammes of the cheese was cut up into small cubes, placed into a percolator, covered with distilled water and allowed to digest at ordinary temperatures for several hours. The aqueous extract was then withdrawn and more water added, a little at a time, until about one litre of percolate was obtained. This was rendered alkaline with sodium carbonate, extracted with half its volume of Squibb's ether and the ether allowed to evaporate spontaneously. After complete evaporation of the ether the aqueous residue was subjected to the following tests:

One drop was added to a mixture of ferric chloride and potassium ferricyanide. In all cases an immediate precipitate of Prussian blue was formed.

One or two drops were added to a mixture consisting of a few drops each of carbolic acid and strong sulphuric acid. A reddish-yellow coloration ensued in all cases. On standing for several hours this color changed to permanent violet.

The remainder of the aqueous residue was, at a single dose, given to a small kitten. In no case could any ill effects be observed. Since tyrotoxin has been shown by Dr. Vaughan to be such an active poison, and since the physiological test in all cases examined by the writer have been signal failures, it was concluded

that the reactions mentioned above must have been due to other causes. In looking for these causes, it was found that commercial butyric acid could be made to produce both reactions in a satisfactory manner, as will be seen from the following tests:

A single drop of the butyric acid produced only a slight formation of prussian blue when added to a mixture of ferric chloride and potassium ferrieyanide. With a single drop of the butyric acid, the carbolic acid reaction was very marked, the mixture immediately turning bright orange red, and changing to dark violet on standing.

One-half cubic centimetre of the butyric acid was mixed with 50 c. c. of water and filtered. The filtrate was rendered strongly alkaline with sodium carbonate, extracted with ether and the ether was allowed to evaporate spontaneously. The aqueous residue gave both reactions with marked distinctness.

Again, the last sample of cheese examined was allowed to remain in the percolator. The bottom of the percolator was corked, the cheese covered with distilled water and the mouth of the percolator covered with a glass plate. After standing four or five days further, decomposition had set in. The aqueous extract was then withdrawn and filtered. The filtrate was alkaline and had an offensive odor. It was placed in a flask connected with a condenser and a portion distilled over. This was done to destroy any tyrotoxon that might have been present. The distillate was very alkaline and had a strong, sickening odor of herring brine, probably due to trimethylamine. From this distillate both reactions were obtained, the prussian blue reaction being especially marked.

The residue left in the flask was removed, acidulated with sulphuric acid and filtered. The filtrate was again subjected to distillation. The distillate was acid and had a strong odor of butyric acid. It gave no prussian blue reaction and only a faint one with carbolic acid. A portion of this distillate was rendered alkaline with sodium carbonate and extracted with ether. The residue gave no reaction whatever with carbolic acid, owing evidently to the fact that the sodium butyrate is insoluble in ether. The remainder of the acid distillate was then mixed with the alkaline distillate obtained above. The mixture was rendered alkaline

with sodium carbonate and then extracted with ether. The aqueous residue now gave both reactions very distinctly.

From these experiments it may be inferred :

1. That the prussian blue reaction is caused by the presence of an organic base, probably an amine.
2. That the carbolic acid reaction is due to butyric acid.
3. That, when both bodies are present in the same liquid both are extracted with ether from an alkaline solution, probably in the form of a butyrate of the organic base.
4. That both bodies are liable to occur in any old specimen of cheese, milk or cream.
5. That the presence of these two bodies causes artificial diazobenzole to give the orange red reaction with carbolic acid, after being extracted from whey with ether, which it does not give before.

THE RELATIVE MERITS OF THE WANKLYN AND THE  
ADAMS METHODS IN THE ESTIMATION OF  
FAT IN MILK ANALYSIS.

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BY JOSEPH F. GEISLER.

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The enactment of laws regulating the quality of milk necessarily involves the adoption of minimum limits or standards. The analytical methods used to ascertain the data must be practical and accurate, and must not involve too great an expenditure of time. Since the adoption of milk standards, especially the minimum limits as to solids and fat, many methods of more or less merit have come into use. The method of Wanklyn, with slight modifications, has been most generally adopted, and in fact has served in determining the standards in many countries. Up to the time of the introduction of the Adams or *coil method*, it was generally considered that the Wanklyn method, and the gypsum or sand methods, gave sufficiently accurate results for all practical purposes. This opinion is still retained by some chemists. The extensive introduction of the coil method and the exhaustive investigations by the Society of Public Analysts in England called attention to great discrepancies between the per cents. of fat ascertained by the coil method and those determined by other methods. It has been generally supposed that the Adams method would usually extract 0.2 to 0.4 per cent. more fat than could be found by the Wanklyn method.

Those who have had experience in the analysis of a great variety of milk and who have made comparative tests by the different analytical methods, have probably obtained differences greater than these.

Having made many such comparative analyses I present herewith some of the analytical data obtained in the analysis of both pure and adulterated milk.

## THE WANKLYN METHOD.

In this method about five (5) cubic centimetres of milk are accurately weighed in a tared platinum (flat bottomed) dish and then dried at a temperature of 100° C. to practically constant weight. The dry residue is then exhausted by repeated portions of boiling ether, or petroleum ether, and the extracted fat weighed direct or by difference, *i. e.*, loss in weight of the dry residue first obtained. Carefully worked the duplicate determinations of the per cent. of fat agree well with each other. Unless the dry residue be thoroughly broken up with a glass rod during the treatment with ether the results are, at times, liable to fall considerably below the truth, as will be shown in the comparative analyses cited below.

The platinum dishes used are usually of 1½ inches diameter at the base, or the bottom presents about 2 square inches of surface over which the milk solids forming the dry residue are distributed. There are many reasons for the opinion that the fat cannot all be extracted from such a residue by a solvent without first breaking up the residue mechanically. Quite a number of circumstances may influence the results obtained. Milk is extremely variable in composition. Not only does the fat vary widely in percentages, but the other constituents, and the relative proportions of these to one another, may also vary considerably at times. These, together with the fact that there is considerable difference in the size of the fat globules of the milk of different breeds of cows, are the main causes. It must be quite generally known to those who handle milks to any extent that the individual fat globules of the milk of Jersey cows are considerably larger than those of the milk of Holsteins. For this reason the cream from the milk of the former rises much more quickly and perfectly. This illustration applies to other milks as well. During the evaporation of the milk in the flat bottomed platinum dish the bulk of the fat rises to the surface and forms a layer from which the fat is easily dissolved by the given solvent. The more perfect the initial separation, the more complete and perfect will be the subsequent exhaustion on the application of the proper solvents. There is, however, good reason to believe that in some milks, owing to peculiar combinations of conditions, considerable fat is retained in the



dry residue, so completely incased in the hardened sugar and casein that it is impossible for the solvent to get at it in this condition. Such a residue when pulverized will frequently be found to yield 0.3 to .4 per cent. more fat.

That there is great variation in the time required for the cream to rise in different milks is a fact quite well known. In the author's experience a sample of milk was brought to him as a skimmed milk having shown but very little cream by the cream test. The sample upon analysis was found to contain over 4 per cent. of fat.

#### THE ADAMS OR COIL METHOD.

In this method many mechanical difficulties are overcome and the data obtained answer all requirements as to accuracy. The method is used principally in the estimation of *fat*. It is a vast improvement over the Wanklyn and similar methods inasmuch as the milk solids are distributed over so large a surface that the solvents used are enabled to extract *all* the fat. The method is, briefly, as follows:

White demy blotting paper, mill 428, weighing about 38 pounds per ream is cut into strips 22 inches long and  $2\frac{1}{4}$  inches wide. Each strip is rolled into a loose helical coil having a diameter a little less than an inch. The coils must be exhausted with ether and finally dried at 100° C.

"The milk to be examined is shaken, and with a pipette, 5 c.c. are discharged into a small beaker 2 inches high by  $1\frac{1}{4}$  diameter, of a capacity of about 30 c.c., weighing about 12 grams. This charged beaker is first weighed, and then a paper coil gently thrust into the milk very nearly to the bottom. In a few minutes the paper sucks up nearly the whole of the milk. The paper is then withdrawn by the dry extremity of the coil and gently reversed, and stood dry end downwards on a clean sheet of glass. With a little dexterity all but the last fraction of a drop can be removed from the beaker and got upon the paper. The beaker is then again weighed, and the milk taken estimated by difference. It is of importance to take up the whole of the milk from the beaker, as I am disposed to consider that the paper has a selective action, removing the water constituents of the milk by preference over the fat.

“The charged paper is next placed in the water oven on the glass plate, milk-end upwards, and roughly dried. Mismanagement may possibly cause a drop to pass down through the coil on to the glass. This accident ought never to occur, but if it does, it is revealed in a moment by inspection of the surface of glass, and the experiment is thereby lost. In about an hour it is rough-dried and in a suitable condition for the extraction of the fat.”

Many modifications have been introduced but only in minor details. Some chemists use a different filter paper, others use asbestos fibre or asbestos paper. The use of coils of a good quality of filter paper has the advantage of exposing comparatively a very large surface over which the dry milk solids are distributed and thus exposed to the action of the solvent. A paper  $22\frac{1}{2} \times 2\frac{1}{2}$  inches has at least  $56\frac{1}{4}$  sq. in. surface, or  $112\frac{1}{2}$  sq. in. for the two sides, as the smallest surface exposed. When it is further considered that the milk is distributed over the individual fibers of the paper it is at once seen that the surface is still more increased. It is probable that the surface thus exposed in a coil ranges from 300 to 400 square inches. This large surface enables the complete extraction of the fat in the shortest possible time.

I have preferred to modify the details somewhat as follows :

The coils\* are prepared from Schleicher & Schüll's filter paper No. 597, the strips cut to the usual size  $22\frac{1}{2} \times 2\frac{1}{2}$  inches. The coils are thoroughly exhausted by repercolation with hot ether, and when necessary also with hot alcohol, until all soluble matter has been extracted, then dried and kept ready for use. For an analysis a coil is unrolled, the edges turned up about  $\frac{1}{4}$  inch for the full length of the strip, and then, by suitably fastening the ends, it is hung up at an angle of about 45 deg. Into a small tared beaker of about 18 c.c. capacity, about 6 c.c. of milk are accurately weighed and then immediately transferred to the inclined strip by gradually dropping the milk upon the same. The beaker and glass rod are then wiped dry with a small piece of filter paper and this is hung up with the strip. In this manner with a little care

\* S. & S. now manufacture specially for milk analysis a grade of paper, No. 571, which is guaranteed free from fat.

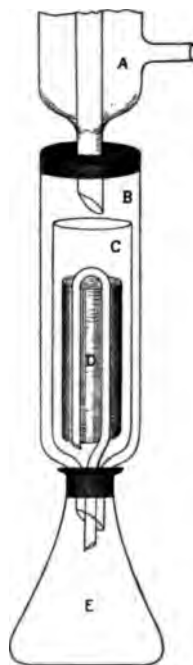
not a particle of the weighed quantity of milk taken need be lost. The coil, before the milk is transferred to the same, is marked with a number agreeing with the number of the milk sample so that it can be indentified. It is then hung perpendicular and allowed to hang for 1 to 3 hours until dry, finally rolled into a loose coil and transferred to an air bath and dried at 100° C., for about  $\frac{3}{4}$  hour to 1 hour or until thoroughly dry. The coil is then transferred to a repercolation apparatus having an intermittent syphon in which the constant repercolation of the ether extracts all the fat from the coil.\*

When the extraction is complete the coil is removed, the ether recovered, and the residual fat remaining in the tared flask first dried a few minutes on the water bath, the flask wiped off clean and dry, transferred to an air bath, dried at 100° C. for 20 to 30 minutes, and, after cooling 10 to 15 minutes, weighed. To ensure accuracy it is well to dry the flask a second time for about 20 minutes and reweigh as before.

The washed ether used for such extractions must be redistilled or tested, to make sure that it does not yield any residue, which would otherwise be calculated as fat. A suitable size of extraction apparatus is described herewith.

\*It is best to cover the top of the coil with a small piece of exhausted filter paper so as to prevent the condensed ether from mechanically removing particles of the solidified material from the coil.

EXTRACTION APPARATUS.\*



A. Liebig Condenser.

B. Percolator. Diameter (int.)  $1\frac{1}{2}$  inches; Length of body,  $6\frac{1}{2}$  to 7 inches. Lower stem about 2 inches long, cut off obliquely, and not less than  $\frac{3}{8}$  inches int. diameter.

C. Extractor. Length of body,  $4\frac{1}{4}$  to  $4\frac{1}{2}$  inches, internal diameter, 1 inch. Lower stem about 3 inches long, and cut off obliquely. Internal diameter of lower stem and intermittent syphon, about  $\frac{1}{8}$  inch. Height of syphon,  $3\frac{1}{4}$  to  $3\frac{1}{2}$  inches, with inner end, which must reach to near the bottom of the extractor, cut off obliquely.

D. Coil of paper.

E. Erlenmeyer Flask. Flask about 4 inches high, wide neck, and measuring about 150 c. c.

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\* Although this apparatus was designed by the author, he makes no claim as to originality of the same.

*Analytical Data.*

The following analyses were made by the "Wanklyn" method. In the series *A* petroleum ether was used for the fat extraction and in the duplicates, series *B*, purified ether. It will be observed that there is no material difference in the percentages of fat obtained, so that either answers equally well as a solvent.

<i>A</i>	No. 1.	<i>B</i> , duplicate
Spec. Grav. at 15.5° C.	—1.0261—	
Water.....89.442%		89.446%
Total Solids.....10.558%		10.554
100.000%		100.000
Fat.....3.056		3.038
Casein and Sugar...6.931		6.924
Ash......571		.592
Total Solids.....10.558%		10.554%
	No. 2.	
Sp. Gr. at 15.5° C.	—1.030—	
Water.....88.518		88.527
Total Solids.....11.482		11.473
100.000		100.000
Fat.....3.243		3.240
Casein and Sugar...7.582		7.568
Ash......657		.665
Total Solids.....11.482%		11.473%
	No. 3.	
Sp. Gr. at 15.5° C.	—1.025—	
Water.....89.240		89.227
Total Solids.....10.760		10.773
100.000		100.000
Fat.....3.588		3.488
Casein and Sugar...6.572		6.678
Ash......600		.607
Total Solids.....10.760%		10.773%

In the above fat determinations, as well as all the following fat estimations by the "Wanklyn method," a glass rod was used to

break up somewhat the hardened residue. From the above duplicate analyses it is quite evident that the duplicate estimations of solids and fat agree well with each other. The use of a glass rod to break up the hardened residue is ruinous to the platinum dishes, and unless that device is resorted to the "total" extraction of the fat is impossible. It has been found that the milk residues, which have been exhausted by merely pouring ether upon them, heating to boiling, pouring off and repeating the operation until the ether fails to extract anything further, still contain fat. This has been demonstrated by pulverizing such a residue and again submitting it to the action of ether.

In the following table of analyses of a miscellaneous lot of milks the estimation of the fat was duplicated by the *coil* method.

Sp. Gravity.	% Water.	% Total Solids.	% Caseine & Sugar.	% Ash.	% Fat. "Wanklyn" method.	% Fat. Coil method.	Dif. in % of Fat.
1.0286	88.744	11.256	7.503	.635	3.118	3.35	+.24
1.0290	89.004	10.996	7.425	.616	2.955	3.14	+.19
1.0273	89.194	10.806	7.062	.585	3.159	3.24	+.08
1.0274	88.771	11.229	7.329	.623	3.277	3.61	+.33
1.0257	89.917	10.083	6.832	.588	2.663	3.01	+.35
1.0289	89.160	10.840	7.521	.651	2.668	2.93	+.26
1.0257	89.791	10.209	7.007	.560	2.642	3.14	+.40
1.0264	89.06	10.94	7.004	.582	3.354	3.57	+.22
1.0330	87.192	12.808	8.655	.710	3.443	3.71	+.27
1.0285	88.509	11.491	7.375	.674	3.442	3.57	+.13
1.0290	88.663	11.337	7.602	.623	3.112	3.34	+.23
1.0288	88.568	11.432	7.415	.682	3.332	3.44	+.11
1.029	89.036	10.964	7.258	.695	3.011	3.14	+.13
1.030	89.255	10.745	7.953	.692	2.100	2.69	+.59
1.0248	88.628	11.372	6.701	.588	4.083	4.28	+.20
1.02919	88.180	11.820	7.875	.595	3.35	3.76	+.41
Duplicate	88.210	11.790	7.863	.587	3.34		
1.0270	85.883	14.117	7.297	.589	6.231	6.310	+.08
Sp. G. not taken	88.407	11.593	7.813	.670	3.110	3.71	+.60
1.0332	87.012	12.988	9.050	.738	3.200	3.79	+.59
1.0245	88.839	11.161	6.846	.595	3.720	4.16	+.44

In the above analyses of 20 milks the average difference amounts to +.294% in favor of the coil method, with the differences ranging from +.08% to +.60%. In the following 5 samples recently analyzed in duplicate by both the Wanklyn and *coil* methods the results were as given below. It must be noted, however, that in these fat determinations by the Wanklyn method the dry residues were not manipulated with a glass rod to any extent, but the fat was "exhausted" by repeated application of boiling ether until the latter failed to extract any more fat. All are the average of duplicate determinations.

Water.	Solids.	Ash.	Wanklyn. Fat.	Coil. Fat.	Difference in % Fat.
87.420	12.580	.753	3.359	3.816	+.457
87.905	12.095	.765	2.905	3.625	+.720
87.102	12.898	.734	4.125	4.707	+.582
87.554	12.446	.750	3.398	3.806	+.408
88.226	11.774	.730	3.030	3.602	+.572

The coil method extracted in the five samples an average of .547% more fat than the Wanklyn, the range being from .408 to .720%. Such differences certainly deserve recognition.

The following investigations were made with a view of determining the merits of some of the objections raised against the *coil* method.

*Amount of Substances Soluble in Ether.*

A paper coil, not previously exhausted by ether, submitted to continuous repercolation in the extraction apparatus for four hours, yielded a residue amounting to 0.008 g., which figured on basis of 6 grms. of milk would have shown a maximum increase of .13% apparently, fat. In another lot of paper (Schleicher & Schülls, No. 597) the *average* of 16 coils amounted to 0.0025 g. per coil, which on the above basis of 6 grms. would show an apparent increase of .041%.

*Rate at which the Fat is Extracted.*

The milk used for this series of tests had the following composition :

	Water.	Total Solids.	Fat.	Cas. and Sugar.	Ash.
(Sp. Gr. 1.0274)....	87.847	12.153	4.294	7.163	.696

The coil used was previously exhausted by both ether and alcohol.

	Total ether used=40 grms.	Milk taken=6.073 grms.	
13 syphonings yielded .....	0.2808 grms. fat	=4.294 % fat.	
6 additional syphonings yielded.....	0.0003 " "	=0.004 % "	
6 " " " " .....	0.0000 " "	=0.0 "	
		<hr/>	
		4.298 % fat.	

In this case, therefore, thirteen syphonings extracted practically all the fat, and the additional twelve syphonings yielded scarcely a weighable quantity of anything, which goes to show that the ether does not extract any appreciable quantity of milk sugar, or milk constituents other than fat. In a number of cases where the coil method seemed to give very high results as to per cent. of fat, the residues of "fat" in the flask were completely soluble in petroleum ether.

*Effect of Dropping or Absorption in the transfer of the Milk to the Coil for the Extraction of Fat.*

A pure milk was used for this test:

	Water.	Total Solids.	Fat.	Cas. & Sug.	Ash.
(Sp. Gr. at 155°C.=1.0815)	86.376	13.624	4.540	8.320	.764
% Fat yielded when milk was absorbed in coil as per Adams.....					=4.550
% Fat yielded when milk was dropped upon the unfurled strip....					=4.530

It is thus seen that the difference here amounted to only 0.020 %, considerably within the limits of experimental error.

*Does the Fat Oxidize during the Drying ?*

Some have tried to account for the increased yield of fat by the coil method by attributing it to oxidation of the fat. Direct experiments fail to prove this, and in fact show that if oxidation does take place it is not appreciable under the conditions of the test. A sample of pure milk was taken for the test:

COMPOSITION.

	Water.	Total Solids.	Fat.	Cas. & Surg.	Ash.
(Sp. Gr. at 15.5°C.=1.033)	86.969	13.031	3.864	8.417	.750

Of this milk three different portions were weighed, transferred to the coil paper as usual by dropping and each treated further as indicated below.



The coils, previous to pouring the milk upon the same, had been extracted with ether and alcohol and dried as usual.

- A. The strip with milk hung up and air dried at the temperature of the atmosphere, about 22° C. for 3 hours.
- B. Dried in open air with the heat from a burner at a temperature of 40° to 55° C. for 4 hours.
- C. First dried same as *B*, but in addition thereto 3½ hours at 100° to 103° C. in an air bath.

If the fat is oxidised during the drying, it is reasonable to expect that the longer the drying and the higher the temperature the greater will be the amount of oxidation and the apparent increase in the percentage of fat obtained. The following data were obtained :

	Milk taken.	Fat obtained by Syphoning.	% Fat.
A.....	5.8875 g.	0.2285 g.	=3.881 %
B.....	6.0325	0.2327 g.	=3.859 %
C.....	6.089	0.2347 g.	=3.854 %

Test *C*, which was subjected to the most thorough drying, gave 0.027 % less fat than *A*, and .005 % less than *B*, all of which are within the limits of experimental error. There is, therefore, no evidence that any increase in fat was caused by oxidation, in fact according to the above data the reverse would be the case. It was also found that drying the fat contained in the Erlenmeyer flask in the air bath for 30 to 45 minutes did not give any evidence of oxidation of the fat.

#### INFLUENCE OF THE EXHAUSTION OF THE COILS BY ETHER AND ALCOHOL.

For this purpose coils (S. + S. 597 paper) were prepared by exhausting them for 2 hours in the repercolation apparatus and then dried = "ether" coils.

Some of the "ether" coils were then exhausted by repercolation with hot alcohol and dried = "alcohol" coils.

The milk used in the first series had the following composition :

	Water.	Tol. Solids.	Cas. & Sugar.	Fat.	Ash.
(Sp. Gr. at 15.5 % = 1.0318)	87.155	12.845	8.195	3.890	.760

		Milk taken.	Fat obtained.	% Fat.	Average.
"Ether"	{ No. 1	6.178g	0.2414g	= 3.907%	} 3.917%
Coils	{ No. 2 duplic.	6.017g	0.2363g	= 3.927%	
"Alcohol"	{ No. 3	6.045	0.2337g	= 3.866%	} 3.864%
	{ No. 4 duplic.	6.004	0.2319g	= 3.862%	

Average difference = .053%

The milk for the second series contained :

		Water.	Tot. Solids.	Cas. & Sugar.	Fat.	Ash.
(Sp. Gr. at 15.5° = 1.0312)		87.152	12.848	7.928	4.181	.739%
		Milk taken.	Fat obtained.	% Fat.	Average.	
"Ether"	{ No. 5	6.000	0.2509	= 4.181%	} 4.197%	
Coils	{ No. 6 duplic.	6.0635	0.2555	= 4.213%		
"Alcohol"	{ No. 7	6.1195	0.2524	= 4.124%	} 4.152%	
	{ No. 8	5.946	0.2486	= 4.180%		

Average difference = .045%

A comparison of the above data will show the fact that coils prepared from S. & S. filter paper No. 597 and thoroughly exhausted by ether answer for all practical purposes, the difference of .045% and .053% as above obtained being quite insignificant. As already stated each lot of paper must be tested to guard against error.

I append herewith a number of results of duplicate estimations of fat by the coil method.

% Fat		% Fat	
Miscellaneous Milk		Skimmed Milk	
a.	b. duplicate.	a.	b. duplicate.
		0.345	0.343
3.831	3.855	0.319	0.351
3.828	3.847	0.305	0.302
3.691	3.604	0.502	0.505*
3.876	3.842	0.484	0.508*
2.801	2.776*	0.672	0.694
5.342	5.394**	0.601	0.568

\*<sub>1</sub> An adulterated milk.\*<sub>2</sub> A pure sample of milk from a herd of 6 cows fed on some bran and pasture. The analysis of the milk showed

Water.	Total Solid.	Fat.	Cas. & Sug.	Ash.
85.838%	14.162%	5.368	8.058	.736

This milk was very high colored, owing to the richness in fat. The Sp. Gr. of the milk at 15.5° C. was found to be 1.0305.

\*<sub>3</sub> In these skimmed milks the Wanklyn method failed to show more than .15% fat.

## SUMMARY.

In the data presented most of the data are stated with three decimal figures. It is almost needless to add that beyond the second decimal the figures have but little practical value except in making up averages, but the figures were here retained so as to agree with the data of other tables in which some of the results had to be used.

Attention should also be called to the distinction between the terms—"Wanklyn" and—Wanklyn—method as used throughout the article. In the "Wanklyn" method the dry milk residues were more or less broken up by means of a glass rod, while in the—Wanklyn method no particular attempt is made to mechanically break up the residue during the action of the solvent.

As to the relative merits of the Wanklyn and Adams, or coil method, for the extraction of the fat of milk it must be conceded:

(1) That the duplicates by either method agree well with each other.

(2) That the Adams' or coil method may yield as much as 0.72, per cent. more fat than the Wanklyn method, the variation, depending much upon whether or not the dried residue of milk solids in the Wanklyn method is mechanically broken up during the action of the solvent.

(3) That the *ratio of fat extracted by the Wanklyn method* (or similar methods) *does not bear a uniform ratio to the total percentage of fat contained in the milk*, which fact in itself is sufficient to condemn the method where accuracy is required.

Milk analyzed by the Adams' or coil method should be required to show at least 0.35 per cent. more fat than the standard adopted for the Wanklyn method. From the fact that the coil method extracts more fat than the Wanklyn method it is evident that by the former the "solids not fat" will be found to be lower, frequently as low as 8.5 per cent. In several instances in the pure milk of cows fed on grass pastures the "solids not fat" were found as low as 8.30 to 8.00 per cent.

Although the *average* difference between the Wanklyn and the Adams' (or coil) method may be considered as 0.3 to 0.5 per cent., yet it must be borne in mind that *averages* cover up a multitude of sins and that it is the extremes we must guard against.

## ABSTRACTS.

### ANALYTICAL CHEMISTRY.

#### Analysis of the Barium Group. By DR. C. LÜDEKING.

The author finds that in the customary test with calcium sulphate solution for barium and strontium, considerable quantities of these may be overlooked. The limits of precipitation may be seen in the following table:

Quant. of Chloride.	Dissolved in Water c. c.	Reagent.	Remarks.
1. 0.003g Ba	2 c. c.	1 c. c. Ca SO <sub>4</sub> sol.	Definite precipitation.
2. 0.002g Ba	2 c. c.	“ “	Precip. only after standing some time.
3. 0.001g Ba	3 c. c.	1 gtt. K <sub>2</sub> CrO <sub>4</sub> sol.	Precipitate.
4. 0.020g Ba ) 0.986g Ca {	4 c. c.	1 c. c. Ca SO <sub>4</sub> sol.	No precipitate.
5. 0.003g Ba ) 0.986g Ca {	2 c. c.	3 c. c. Sod. Acetate sol. 2 c. c. K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> sol.	No precipitate in cold, but after boiling.
6. 0.010g Ba ) 0.986g Ca {	13 c. c.	1 c. c. Ca SO <sub>4</sub> sol.	No precip. Precip. on addition of K <sub>2</sub> CrO <sub>4</sub>
7. 0.001g Sr	2 c. c.	1 c. c. Ca SO <sub>4</sub> sol.	No immediate precip. on boiling. Precip. after 15 minutes.
8. 0.002g Sr	2 c. c.	1 c. c. Ca SO <sub>4</sub> sol.	Immediate precip. on boiling.

Calcium chloride was found to interfere very much with the precipitation of strontium by Ca SO<sub>4</sub> solution.

A solution containing 30% of Sr Cl<sub>2</sub>.6H<sub>2</sub>O is precipitated by Ca SO<sub>4</sub> solution in the cold.

Under favorable conditions the author considers .1% Ba Cl<sub>2</sub> and .06% Sr Cl<sub>2</sub> the limits by the calcium sulphate test, while potassium chromate will give a distinct precipitate with a solution containing only .03% of Ba Cl<sub>2</sub>. The reactions are much less delicate when considerable quantities of strontium or calcium chloride are present. It is therefore recommended that the precipitated carbonates of the barium group, after careful washing, be dissolved in acetic acid, and the solution tested with potassium bichromate solution,\* heat if necessary. If a precipitate forms, filter. Examine the precipitate for barium. The filtrate is neutralized with NH<sub>4</sub> OH, precipitated by ammonium carbonate, washed, dissolved in hydrochloric acid and tested for strontium by the spectroscope. Separate the strontium, if present, by means of sulphuric acid, and in the filtrate test as usual for calcium. *Ztschr. anal. Chem.*, 29, 556-561.

J. F. G.

**Reactions of Resorcin and Thymol.** By II. BORNRÄGER.

Resorcin and thymol both give red color reactions with nascent nitrous acid, the former blood red, the latter yellowish red.

In alcoholic solution both remain clear, but in water solution the thymol deposits yellowish red flakes. The thymol also produces an ethereal odor due to formation of thymol nitrite.

Another distinctive test is to place in a test tube about equal quantities of some dry nitrite, calcium sulphate and sodium bisulphate, moisten with water, add the liquid to be tested and heat the mixture. In presence of thymol the mixture becomes chrome red, while resorcin gives rise to a dark chrome green color and bright red drops in the upper part of the tube. The solution must be acid to develop the colors. (*Ztschr. anal. Chem.*, 29, 572.)

J. F. G.

**Estimation of Zinc in its Ores.** By DELFO CODA.

In the customary method for estimating zinc in its ores considerable zinc is lost by being enclosed in the precipitated iron

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\* This method of separation is not new, as it has been used by the students from the laboratory of the Univ. of Michigan, for over ten years. See also "Qualitative Chemical Analysis," by Douglas & Prescott, 3d Ed., p. 242

J. F. G.

from which it is not totally removed by washing. To prevent this loss the author recommends ammonium sulphate.

Dissolve 2.5g zinc ore in 15 to 20 c.c. aqua regia, evaporate, add 15-20 c.c.  $\text{H}_2\text{SO}_4$ , heat until sulphuric acid vapors rise so as to ensure removal of Cl and NO. In presence of Cu, Cd., etc., dilute and precipitate by  $\text{H}_2\text{S}$ , filter and remove  $\text{H}_2\text{S}$  from filtrate by boiling. The filtrate containing Zn, Fe, Mn and alkalies; neutralize with ammonia, then add 40 c.c. ammonia (10%?), containing one-quarter ammonium carbonate. The iron is precipitated free from zinc. Cool, dilute to 500 c.c., filter through a dry filter and of the filtrate take portions of 100 c.c., dilute each to 250 c.c. This solution is ready for titration with sodium sulphide solution.

For comparison or standardizing dissolve a known weight of zinc (the quantity should be about that contained in .5 gm. of the zinc ore under examination) in 4 c.c. hydrochloric acid, dilute, make alkaline with 20 c.c. ammonia, dilute again to 250 c.c. For precipitation use a 2% solution of crystallized sodium sulphide, using sodium nitroprusside as an indicator of the end reaction. The several portions of 100 c. c. each serve for checks upon each other in the titration. (*Ztschr. anal. Chem.*, 29, 266-271.) J. F. G.

#### Examination of Alcoholic Liquors. By W. FRESSENIUS.

A lengthy and valuable paper on the examination and appraising of alcoholic liquors. The article does not admit of a brief abstract, hence the readers are referred to the original. (*Ztschr. anal. Chem.*, 29, 283-317.) J. F. G.

#### Valuation of Zinc Dust. By G. KLEMP.

The author bases his method upon the reduction of iodic acid in alkaline solution. The comparative estimations with other methods gave very satisfactory results. Metallic iron and lead will always interfere more or less with oxidation and reduction methods.

Requirements :

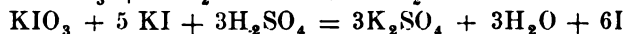
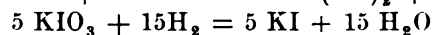
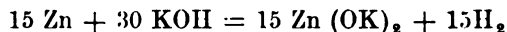
A solution of 15.25 grms.  $\text{KIO}_3$  in 300 c. c. of water, of which solution 3 c. c. are used for each 0.1 gm. zinc dust taken.

An alkaline solution containing either 300 grms. NaOH, or about 370 grms. KOH per litre, of which 10 c. c. are to be used for each 0.1 gm. zinc.

Of the finely divided and carefully mixed dust weigh out 0.5 to 1 gm. into a dry glass stoppered flask of about 200 c. c. capacity. Mix the required amounts of KOH and KIO<sub>3</sub> solutions (10 c. c. of the former, and 3 c. c. of the latter for each 0.1 gm. zinc taken) in a beaker, and after adding a few glass beads to the zinc in the flask, pour in the alkaline mixture, stopper securely, and agitate the contents of the flask for about five minutes. Cool before removing the stopper. \* Remove the contents of the flask to one of 250 to 500 capacity, according to the quantity of zinc taken. Fill up to mark after cooling and contraction has taken place upon diluting the solution. Mix thoroughly and remove 100 c. c. to a suitable retort for distillation. It is essential that cork and rubber stoppers be avoided, hence, the ground stopper end of the retort must be carefully fitted to the receiver used. In the latter there are placed for 100 c. c. sol., when .5 gm. zinc was taken, 20 c. c. of a solution containing .4 gm. KI. Through a funnel dilute sulphuric acid is added to the contents in the retort and the latter immediately connected with a CO<sub>2</sub> apparatus. Heat is now gradually applied to the retort until the contents boil actively.

Distillation is usually completed in about 20 minutes. It is well to protect the receiver with a safety tube containing KI sol. so as to prevent loss of I, which may be carried over by the CO<sub>2</sub> current. A suitable apparatus is that of Topf (*Ztschr. anal. Chem.*, **26**, 293). The liberated iodine is estimated volumetrically by means of sod. hyposulphite sol.

The reactions are based upon the equations :

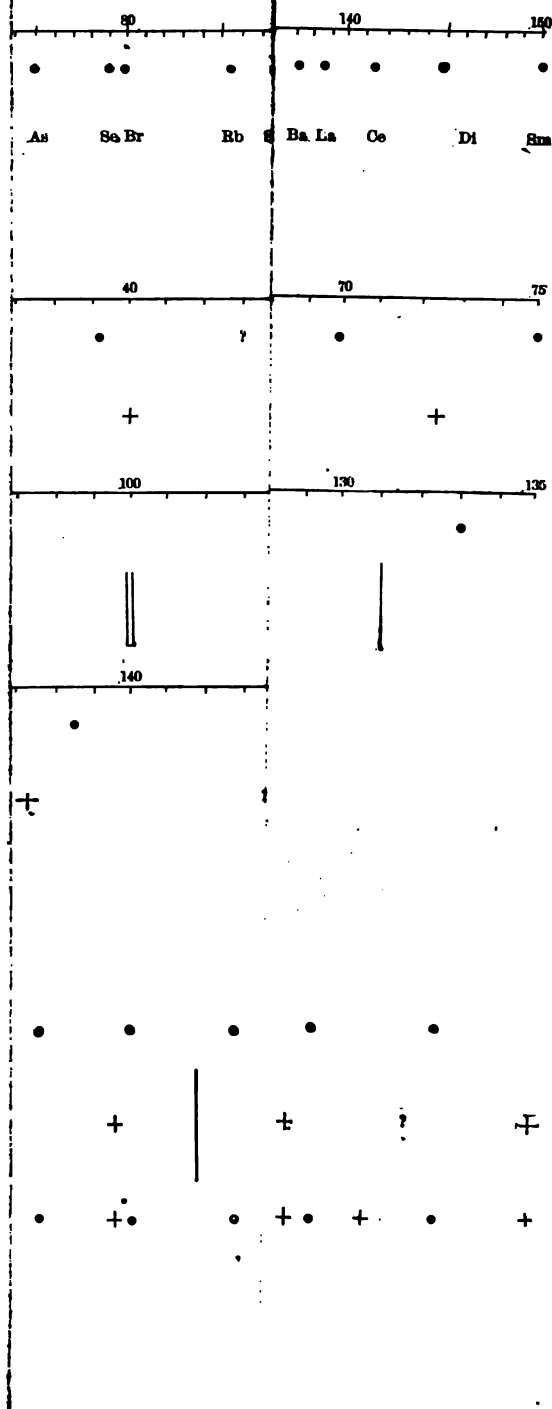


Whence 5 Zn = 2I or 0.1 gm. Zn = 0.407,799 gm. I (*Ztschr. anal. Chem.*, **29**, 253-266) J. F. G.

---

\* It is better at once to place the zinc in a flask of suitable size so as to avoid the transfer. J. F. G.

PERISSAD LAW.  
PLATE I.



On account of slight errors in this plate as printed in Nov. No. facing page 430, a corrected copy is furnished herewith at the request of the author.—Ed.



1

2

3

## Abstracts of American Patents Relating to Chemistry.

(From the U. S. Patent Office Gazette.)

*Issued December 2, 1890.*

**441,803.**—Preparing acidulated oil. H. Nordlinger.

A process of obtaining a homogeneous mixture of fatty oil and vinegar free from water and other impurities, consisting in first mixing the oil and vinegar, next adding a salt soluble in water to throw down the water and other impurities from the oil and vinegar, and afterwards separating by decantation the acidulated oil from the impurities and saline liquid.

**441,853.**—Manufacture of varnish. B. Piffard.

A varnish consisting of colophionate of lead, wax or waxy matter, and a solvent.

**441,941.**—Gas producer. J. W. Culmer.

**441,945.**—Red dye. C. Dreyfus.

Prepared by combining diazotized dehydrothioparatoluidine sulphonic acid with beta naphthol.

**442,016.**—Process of treating ore containing lead, silver and zinc. C. L. Coffin.

*Issued December 9, 1890.*

**442,094** —Sulpho compound. E. A. Baumann.

A compound having the formula  $C_9S_2O_4H_{10}$ , melting at  $87^\circ C.$ , crystallizing in silvery scales, difficultly soluble in cold water, easily in hot water, ether, alcohol and benzine.

**442,109.**—Process of making chromates. W. J. A. Donald.

The process consists in calcining the insoluble residuum, resulting from the ordinary manufacture of chromates, pulverizing it, and then mixing this powder with chrome ore, lime, and a solution of the salt to be produced.

**442,164.**—Quick match. L. Bäärnhelm.

Consists of a core of twisted cotton yarn impregnated with a solution of potassium chlorate, to which is added potassium ferrocyanide, and coated with collodion and directly surrounded with an envelope of asphalt, dissolved in linseed oil or another fat oil, to which likewise is added some salt of manganese protoxide, talc and sulphur.

**442,195.**—Paint. J. T. McKim.

Consists of calcareous ochre, iron ore paint, litharge, argol, japan, coal tar and benzine.

**442,245.**—Insect powder. G. Calor.

A mixture of zinc dust and magnesium carbonate.

**442,297.**—Process of bleaching hair. F. G. Wiselogel.

The hair is first thoroughly washed in cold water, and then treated in a bath of hot water containing a small quantity of lime. It is finally placed in a drying apparatus, and a strong current of dry sulphurated air passed through, until it is dry.

**442,369.**—Blue-black dye. Leo Gans.

Derived from amidonaphtholmonosulphonic acid and tetrazodiphenyl or homologous compounds, soluble in water and nearly insoluble in alcohol, turning blue in sulphuric acid.

**442,397.**—Filter. H. Roeske.

**442,450.**—Process of making iron prints by photography. C. B. McBlair.

The material is sensitized with a solution of ferric chloride, tartaric acid, and ferrous sulphate, and after exposure is developed with gallic acid.

**442,463.**—Composition for fixing ink impressions. D. C. Simpson.

A mixture of plumbic acetate, potassium chlorate and cupric acetate, for treating paper and the like to render writings or markings indelible.

**442,490.**—Process of making fertilizer from sewage sludge. C. H. Morgan.

**442,493.**—Apparatus for the manufacture of wood and oil gas. G. Ramsdell.

**442,593.**—Food product. A. W. Rehnstrom.

Consists of dry and roasted whey and milk.

*(Issued December 16, 1890.)*

**442,600.**—Apparatus for utilizing waste gaseous products. E. Biedermann and E. W. Harvey.

**442,601.**—Apparatus for filtering water. J. H. Blessing.

**442,602.**—Water filtering apparatus. J. H. Blessing.

**442,613.**—Regenerative gas lamp. L. A. Cooper.

**442,625.**—Ammonia still. F. Kaiser.

**442,628.**—Apparatus for dyeing hides. J. Kristen.

**442,661.**—Process for desilverizing lead by electrolysis. T. D. Bottome.

Argentiferous lead is subjected to electrolysis, while immersed in an electrolyte composed of ammonium salts kept saturated with carbon dioxide.

**442,680.**—Blue dye. M. Hoffmann and A. Weinberg.

It forms a dark greenish or crystalline powder; dissolves easily in water

with a blue color ; is soluble in alcohol and insoluble in benzine or ether ; dissolves in strong sulphuric acid with a brown shade.

**442,684.**—Tanning process. A. F. Krueger.

The hides are subjected to the action of alum, salt, and cutch, and then to the action of bark liquor.

**442,698.**—Vapor burner. E. G. Mummery.

**442,741.**—Method of manufacturing highly sensitive isochromatic gelatine plates. H. W. Vogel.

Consists of a base, a sensitive film, and a compound of silver, and a dye or dyes held by the film.

**442,802.**—Process of refining hydrocarbon oils. J. Gardner and J. F. Harris.

**442,867.**—Preservative compound for brick, stone, etc. L. B. Drake.

Consists of boiled linseed oil, water, gasoline, sal soda, sugar of lead, and silicate of soda.

**442,896.**—Oil filter or separator. J. Johnson.

**442,943.**—Manufacture of white lead. G. Bischof.

White lead is prepared from the lead oxides of commerce by reducing them to suboxide, then subjecting the latter, mixed with water, to the action of the air, and finally subjecting the resulting product in admixture with water, sugar and acetic acid or an acetate to the action of carbon dioxide.

**442,962.**—Hydrometer. A. Eichhorn.

A hydrometer having a picnometer suspended from the float.

**443,026.**—Dye. F. C. Weiss.

The materials to be dyed are treated with anacardine extract, potassium birchromate and indigo.

**443,035.**—Dynamite. W. D. Borland.

A liquid nitro explosive absorbed by charred or carbonized cork.

*(Issued December 23, 1890.)*

**443,105.**—Method of preparing nitro-cellulose. G. M. Mowbray.

The process consists of three steps: first, a preliminary impregnation of the cellulose material, whether simply fibrous, felted, or textile, by crystallizing a salt, preferably sodium nitrate, in the interstices of the cellulose material ; second, immersing this dry saline impregnated cellulose material in a suitable bath of sulphuric and nitric acids ; and, third, removing the nitro-cellulose from the saline acid bath, washing out the adherent acids, and drying the nitro-cellulose.

**443,116.**—White safety paper. A. Schlumberger.

The paper is impregnated with a resinated ferrous salt, a resin compound of plumbic ferrocyanide, and a resin compound of manganese ferrocyanide, in combination with a salt of molybdenum and a resin compound of zinc sulphide.

**443,122.**—Process of manufacturing gas. L. Stevens.

**443,153.**—Apparatus for the manufacture of coal gas. J. J. Thomas.

**443,186.**—Purifying water for boilers and salt making. J. L. Alberger.

**443,190.**—Apparatus for the manufacture of fermented liquids. H. Goetter.

**443,225.**—Process of preparing hydrocarbon and other oils for burning. J. H. Macy.

**443,238.**—Process of treating wood and fibre. W. A. Horrall.

The plants are subjected to the action of a liquid composed of water, alcohol, sugar and an acid, until fermentation subsides and disintegration is complete.

**443,250.**—Artificial stone. G. Buchner.

Consists of sawdust, caseine, glycerine, water glass, slaked lime, magnesia, and oil.

**443,328.**—Apparatus for distilling hydrocarbons. T. McGowan.

**443,361.**—Composition for coloring and tinting. F. W. Fewins.

Consists of water, whiting or other water color mineral, soluble glass, boiled linseed oil, and coloring matter.

**443,375.**—Process of marking textile fabrics. D. S. Oliphant.

A solution of potassium bichromate, mucilage and water is applied to the fabric, and after drying it is written upon with an ink consisting of aniline hydrochloride, water, mucilage and glycerine.

**443,402.**—Gallacetophenone. M. V. Nencki.

It is characterized by the following properties: It is a pale, yellowish crystalline substance soluble in hot water, from which it crystallizes on cooling; it is readily soluble in alcohol; in cold benzine it is practically insoluble, and only very slightly soluble in boiling benzine, but soluble in alkalies, giving pale yellow solutions, which soon turn brown on exposure to air; it melts at about 168°C., and on analysis gives figures corresponding to  $C_8H^8O_4$ .

**443,408.**—Yellow-red dye. C. Schraube.

A derivative of rosinduline sulpho acid, which appears as a reddish brown powder, readily soluble in both hot and cold water, giving a yellowish red solution. It is soluble in boiling alcohol, but insoluble in benzene. Large quantities of caustic soda or saturated common salt precipitate it from its aqueous solution. It is soluble in concentrated sulphuric acid, but precipitated by dilute acids.

**443,422.**—Paint. J. H. Baker.

Consists of whiting, glue, alum, plaster of paris, drier, white lead, linseed oil, and water.

**443,464.**—Process of manufacturing steel coated wire. F. Sedgwick.

The surface of a wire is converted into steel by drawing the wire through a steelifying bath or material and heating that portion of the wire which is in the act of passing through the bath or material by means of electricity.

(Issued December 30th, 1890.)

**448,549.**—Apparatus for refining loaf sugar in moulds. C. Steffen.

**448,559.**—Process of making fertilizer from tank water. H. T. Yaryan.

The tank water is evaporated to the desired density and passed through a dializer, by which deliquescent salts are removed, and finally evaporated to dryness.

**448,584.**—Carburetor. E. D. Self.

**448,629.**—Manufacture of flowers of sulphur. E. F. White.

**448,685.**—Process of making alum cake. H. W. Shepard.

Consists in adding to sulphuric acid bauxite or other aluminous material in quantity sufficient to form a basic sulphate of alumina, adding to the hot pasty mass resulting an alkaline or alkaline earthy sulphide and mixing the same therewith in quantity sufficient to reduce the soluble iron in the mixture to the ferrous state, diluting the mass with water, separating the dissolved sulphate from the insoluble impurities of the mixture, and concentrating the solution to form the commercial aluminous cake.

**448,757.**—Process of reducing copper matte. J. E. Gaylord.

**448,758.**—Process of converting copper matte to copper. J. E. Gaylord.

**448,761.**—Process of purifying spent soap lyes. O. C. Hagemann.

To the spent lye is added an acid and an iron salt, such as ferric chloride, and the precipitate thus formed is removed. Then acid is again added, and chlorine, the liquor is heated and air blown through it, after which the precipitate is removed and the liquor neutralized.

**448,907.**—Extracting oil. J. W. Evans.

**448,940.**—Recovering fatty products. M. L. Griffin, E. S. Thayer and E. S. Buffum.

The process is for treating the residuum of scouring suds, etc., and consists in adding acid, mixing therewith a porous and granular substance in sufficient excess to retain its granular shape, and finally treating it with naphtha or carbon disulphide.

**448,943.**—Alloy. I. H. Johannes.

Consists of more than 15% of aluminium, and less than 85% by weight of tin, antimony and lead combined.

**448,951.**—Apparatus for generating illuminating water gas. J. D. Averell.

**448,979.**—Preparing chocolate. V. Tobias and H. Fischer.

Liquid chocolate is prepared by heating whey or poor milk to the boiling point, then adding a mixture of cocoa and sugar, then cooling the mixture and removing the cocoa butter.

W. R.

EXCHANGES RECEIVED BY THE AMERICAN CHEMICAL SOCIETY

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*(To be found in the Library).*

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UNITED STATES. American Chemical Journal.

American Druggist.  
American Gas Light Journal.  
American Journal of Pharmacy.  
American Manufacturer and Iron World.  
American Naturalist.  
Annals of the New York Academy of Sciences.  
Anthony's Photographic Bulletin.  
Bulletin of the American Museum of Natural History.  
Bulletin of the Connecticut Agricultural Experiment Station.  
Bulletin of the Massachusetts State Agricultural Experiment Station.  
Circulars of Information, Bureau of Education, Washington, D. C.  
Deutsch-Amerikanische Apotheker-Zeitung.  
Druggists' Circular.  
Engineering and Mining Journal.  
Ephemeris (Sqibb).  
Journal of Analytical Chemistry.  
Journal of the Franklin Institute.  
Manufacturer and Builder.  
Manufacturers Review and Industrial Record.  
Medico-Legal Journal.  
New Idea.  
New York Medical Journal.  
Oil, Paint and Drug Reporter.  
Pharmaceutical Record.  
Popular Science Monthly.  
Proceedings of the Academy of Natural Sciences, Philadelphia.  
Proceedings of the American Academy of Arts and Sciences, Boston.  
Proceedings of the American Philosophical Society, Philadelphia.

- Reports of the Geological Survey of Pennsylvania.  
Reports of the Storr's School Agricultural Experiment Station.  
School of Mines Quarterly.  
Technology Quarterly.  
Textile Colorist.  
Transactions of the American Institute of Electrical Engineers.  
Transactions of the American Institute of Mining Engineers.  
Transactions of the New York Academy of Sciences.
- CANADA. Proceedings of the Canadian Institute.  
Reports of the Geological Survey of Canada.
- CHILI. Verhandlungen des deutsch-wissenschaftlichen Vereins zu Santiago.
- MEXICO. Boletin del Ministerio de Fomento.  
Boletin Mensual.  
Informes y Documentos Relativos á Comercio, etc.  
Memorias y Revista de la Sociedad Cientifica.
- PERU. Boletin de Minas.
- GREAT BRITAIN. Analyst.  
Chemical News.  
Engineering.  
Industries.  
Invention.  
Iron.  
Journal of the Chemical Society.  
Journal of the Society of Arts.  
Journal of the Society of Chemical Industry.  
Oil and Colorman's Journal.  
Pharmaceutical Journal and Transactions.  
Sugar Cane.  
Transactions of the Laboratory Club.
- FRANCE. Annales des Mines.  
Bulletin de la Société Chimique de Paris.  
Bulletin de la Société Industrielle de Rouen.  
Moniteur de la Teinture.  
Moniteur Scientifique, Quesneville.  
Repertoire de Pharmacy.
- GERMANY. Archiv der Pharmacie.  
Bierbrauer.  
Bulletin de la Société Industrielle de Mulhouse.  
Gerber-Zeitung.  
Sitzungsberichte der K. B. Akademie der Wissenschaften zu Munchen.



- HOLLAND.** Revue International des Falsifications.  
**AUSTRIA.** Allgemeine Oesterreichische Chemiker und Techniker Zeitung.  
Chemisch-Technischer Central-Anzeiger.  
Drogisten Zeitung.  
Jahrbuch de K. K. Geologischen Reichsanstalt.  
Oesterriche Zeitschrift für Berg-und Hüttenwesen.  
**ITALY.** Gazzetta Chimica Italiana.  
**RUSSIA.** Bulletin de l'Academie Imperiale des Sciences de St. Petersburg.  
Memoires de la Société des Naturalistes de Kiew.  
**AUSTRALIA.** Journal and Proceedings of the Royal Society of New South Wales.  
The Australasian Journal of Pharmacy.

### **ERRATA.**

Page 25 ; 15th line from top for *azainine* read *azamine*.

Page 167 ; top—for *of* read *upon*.

Page 277 ; under title of article, insert By A. H. Sabin.

Page 368 ; for Dr. Edward P. *Haws* read *Harris*.

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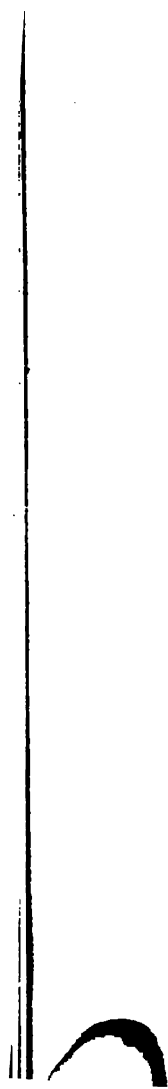
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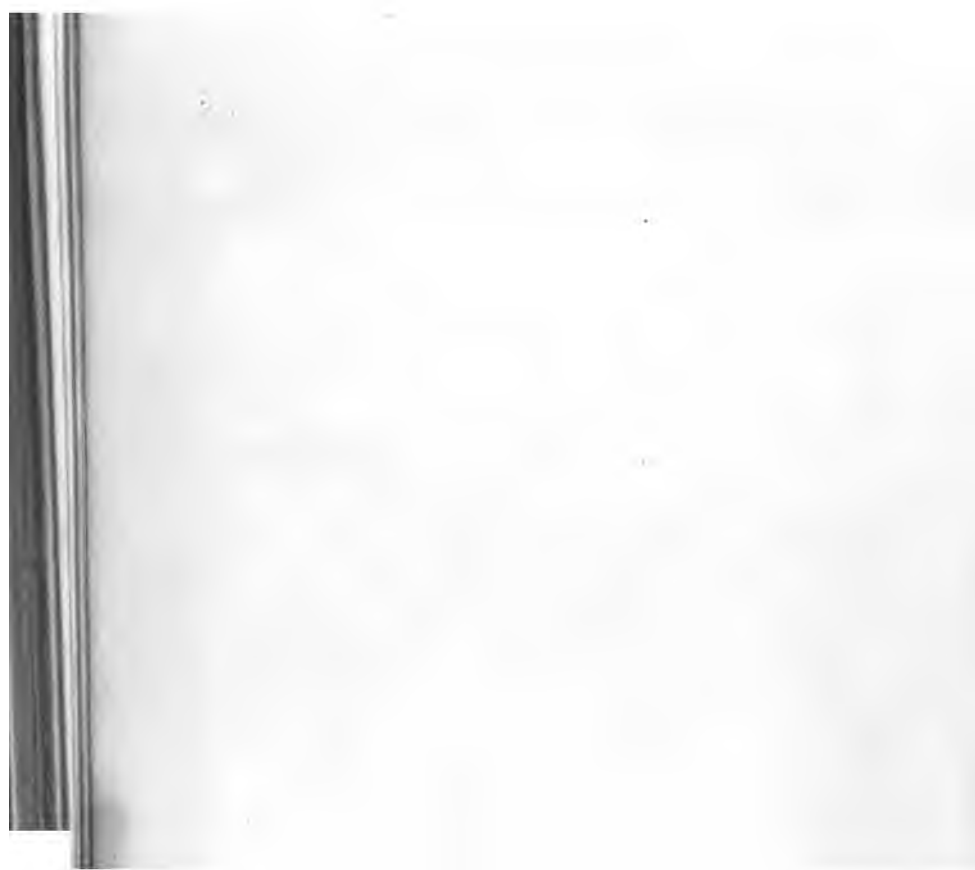
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